CHAPTER 2

ATOMIC STRUCTURE

2.1 INTRODUCTION

The word **atom** is a Greek word meaning indivisible, *i.e.*, an ultimate particle which cannot be further subdivided. The idea that all matter ultimately consists of extremely small particles was conceived by ancient Indian and Greek philosophers. The old concept was put on firm footing by **John Dalton** in the form of **atomic theory** which he developed in the years 1803–1808. This theory was a landmark in the history of chemistry. According to this theory, atom is the smallest indivisible part of matter which takes part in chemical reactions. Atom is neither created nor destroyed. Atoms of the same element are similar in size, mass and characteristics; however, atoms of different elements have different size, mass and characteristics.

In 1833, Michael Faraday showed that there is a relationship between matter and electricity. This was the first major breakthrough to suggest that atom was not a simple indivisible particle of all matter but was made up of smaller particles. Discovery of **electrons, protons** and **neutrons** discarded the indivisible nature of the atom proposed by John Dalton.

The complexity of the atom was further revealed when the following discoveries were made in subsequent years:

(i) Discovery of cathode rays.
(ii) Discovery of positive rays.
(iii) Discovery of X-rays.
(iv) Discovery of radioactivity.
(v) Discovery of isotopes and isobars.
(vi) Discovery of quarks and the new atomic model.

During the past 100 years, scientists have made contributions which helped in the development of modern theory of atomic structure. The works of **J.J. Thomson** and **Ernest Rutherford** actually laid the foundation of the modern picture of the atom. It is now believed that the atom consists of several particles called **subatomic particles** like electron, proton, neutron, positron, neutrino, meson, etc. Out of these particles, the electron, the proton and the neutron are called **fundamental particles** and are the building blocks of the atoms.

2.2 CATHODE RAYS—DISCOVERY OF ELECTRON

The nature and existence of electron was established by experiments on conduction of electricity through gases. In 1859, **Julius Plucker** started the study of conduction of electricity through gases at low pressure in a discharge tube. [A common discharge tube consists of a hard glass cylindrical tube (about 50 cm long) with two metal electrodes sealed on both the ends. It is connected to a side tube through which it can be evacuated to any desired pressure with the help of a vacuum pump.] Air was almost completely removed from the discharge tube (pressure about 10^{-4} atmosphere). When a high voltage of the order of 10,000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrode (Fig. 2.1). Since, the negative electrode is referred to as cathode, these rays were called **cathode rays.**

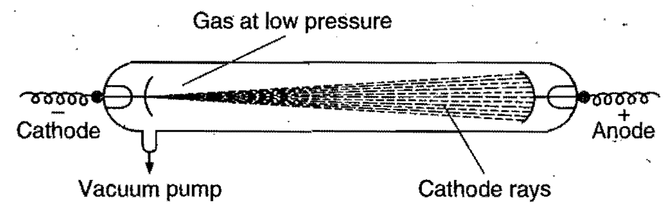


Fig. 2.1 Production of cathode rays

Further investigations were made by W. Crookes, J. Perrin, J.J. Thomson and others. Cathode rays possess the following properties:

(i) They travel in straight lines away from the cathode with very high velocities ranging from $10^9 - 10^{11}$ cm per second. A shadow of metallic object placed in the path is cast on the wall opposite to the cathode.

(ii) They produce a green glow when strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.

(iii) They produce heat energy when they collide with the matter. It shows that cathode rays possess kinetic energy which is converted into heat energy when stopped by matter.

(iv) They are deflected by the electric and magnetic fields. When the rays are passed between two electrically charged plates, these are deflected towards the positively charged plate. They discharge a positively charged gold leaf electroscope. It shows that **cathode rays carry negative charge.**

(v) They possess kinetic energy. It is shown by the experiment that when a small pin wheel is placed in their path, the blades of the wheel are set in motion. Thus, the **cathode rays consist of material particles which have mass and velocity.**

These particles carrying negative charge were called **negatrons** by Thomson.

The name 'negatron' was changed to 'electron' by **Stoney**.

(vi) Cathode rays produce X-rays. When these rays fall on a material having high atomic mass, new type of penetrating rays of very small wavelength are emitted which are called X-rays.

(vii) These rays affect the photographic plate.

(viii) These rays can penetrate through thin foils of solid materials and cause ionisation in gases through which they pass.

(ix) The nature of the cathode rays is independent of:

(a) the nature of the cathode and

(b) the gas in the discharge tube.

In 1897, **J. J. Thomson** determined the e/m value (charge/mass) of the electron by studying the deflections of cathode rays in electric and magnetic fields. The value of e/m has been found to be -1.7588×10^8 coulomb/g.

[The path of an electron in an electric field is parabolic, given as:

$$y = \frac{eE}{2mv^2} x^2$$

where, y = deflection in the path of electron in y-direction
e = charge on electron
E = intensity of applied electric field
m = mass of electron
v = velocity of electron
x = distance between two parallel electric plates within which electron is moving.

The path of an electron in a magnetic field is circular with radius 'r' given as:

$$r = \frac{mv}{eB}$$

where, m = mass of electron
v = velocity of electron
e = charge on electron
B = intensity of applied magnetic field

The radius of the path is proportional to momentum.]

By performing a series of experiments, **Thomson** proved that **whatever be the gas taken in the discharge tube and whatever be the material of the electrodes, the value of e/m is always the same.** Electrons are thus common universal constituents of all atoms.

J.J. Thomson gave following relation to calculate charge/mass ratio:

$$\frac{e}{m} = \frac{E}{rB^2}$$

where the terms have usual significance given before

$$= -1.7588 \times 10^{11} \text{ C kg}^{-1}$$

Electrons are also produced by the action of ultraviolet light or X-rays on a metal and from heated filaments. β-particles emitted by radioactive materials are also electrons.

The first precise measurement of the charge on an electron was made by **Robert A. Millikan** in 1909 by oil drop experiment. The charge on the electron was found to be -1.6022×10^{-19} coulomb. **Since, an electron has the smallest charge known, it was, thus,** designated as unit negative charge.

Mass of the electron: The mass of the electron can be calculated from the value of e/m and the value of e.

$$m = \frac{e}{e/m} = \frac{-1.6022 \times 10^{-19}}{-1.7588 \times 10^8}$$

$$= 9.1096 \times 10^{-28} \text{ g or } 9.1096 \times 10^{-31} \text{ kg}$$

This is termed as the rest mass of the electron, *i.e.*, mass of the electron when moving with low speed. The mass of a moving electron may be calculated by applying the following formula:

$$\text{Mass of moving electron} = \frac{\text{rest mass of electron}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where v is the velocity of the electron and c is the velocity of light. When v becomes equal to c, mass of the moving electron becomes infinity and when the velocity of the electron becomes greater than c, mass of the electron becomes imaginary.

Mass of the electron relative to that of hydrogen atom:

Mass of hydrogen atom = 1.008 amu

$$= 1.008 \times 1.66 \times 10^{-24} \text{ g} \quad (\text{since } 1 \text{ amu} = 1.66 \times 10^{-24} \text{ g})$$

$$= 1.673 \times 10^{-24} \text{ g}$$

$$\frac{\text{Mass of hydrogen atom}}{\text{Mass of the electron}} = \frac{1.673 \times 10^{-24}}{9.1096 \times 10^{-28}}$$

$$= 1837$$

$$\text{Thus, Mass of an electron} = \frac{1}{1837} \times \text{mass of hydrogen atom}$$

$$= \frac{1.008}{1837}$$

$$= 0.000549 \text{ amu}$$

An electron can, thus, be defined as a subatomic particle which carries charge -1.60×10^{-19} coulomb, *i.e.*, one unit negative charge and has mass 9.1×10^{-28} g, *i.e.*, $\frac{1}{1837}$th mass of the hydrogen atom (0.000549 amu).

[Millikan's oil drop method is used to determine the charge on an electron by measuring the terminal velocity of a charged spherical oil drop which is made stationary between two electrodes on which a very high potential is applied.

$$\text{Charge on an electron '}q\text{'} = \frac{6\pi\eta r}{E}(v_1 + v_2)$$

where, η = coefficient of viscosity of the gas medium
v_1, v_2 = terminal velocities
E = field strength
r = radius of the oil drop = $\sqrt{\frac{9\eta v_1}{2(f - \sigma)g}}$

(f = density of oil; σ = density of gas; g = gravitational force)]

2.3 POSITIVE RAYS—DISCOVERY OF PROTON

With the discovery of electrons, scientists started looking for positively charged particles which were naturally expected because matter is electrically neutral under ordinary conditions. The first experiment that led to the discovery of the positive particle was conducted by **Goldstein** in 1886. He used a perforated cathode in the modified cathode ray tube (Fig. 2.2). It was observed that when a high potential difference was applied between the electrodes, not only cathode rays were produced but also a new type of rays were produced simultaneously from anode moving towards cathode and passed through the holes or canals of the cathode. These rays were termed **canal rays** since these passed through the canals of the cathode. These were also named **anode rays** as these originated from anode. When the properties of these rays were studied by Thomson, he observed that these rays consisted of positively charged particles and named them as **positive rays.**

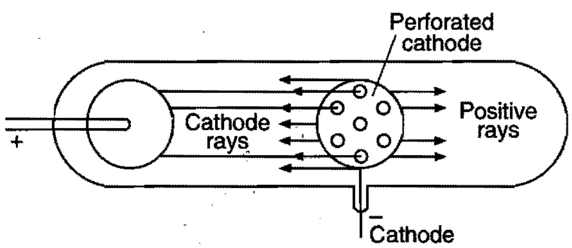


Fig. 2.2

The following characteristics of the positive rays were recognised:

(i) The rays travel in straight lines and cast a shadow of the object placed in their path.

(ii) Like cathode rays, these rays also rotate the wheel placed in their path and also have heating effect. Thus, the rays possess kinetic energy, *i. e.*, mass particles are present.

(iii) The rays produce flashes of light on zinc sulphide screen.

(iv) The rays are deflected by electric and magnetic fields in a direction opposite to that of cathode rays. These rays are attracted towards the negatively charged plate showing thereby that **these rays carry positive charge.**

(v) These rays can pass through thin metal foils.

(vi) These rays can produce ionisation in gases.

(vii) These rays are capable of producing physical and chemical changes.

(viii) Positive particles in these rays have e/m values much smaller than that of electron. This means either m is high or the value of charge is small in comparison to electron. Since, positive particle is formed by the loss of electron or electrons, the charge on the positive particle must be an integral multiple of the charge present on the electron. Hence, for a smaller value of e/m, it is definite that positive particles possess high mass.

(ix) e/m value is dependent on the nature of the gas taken in the discharge tube, *i. e.*, positive particles are different in different gases.

Accurate measurements of the charge and the mass of the particles obtained in the discharge tube containing hydrogen, the lightest of all gases, were made by J.J. Thomson in 1906. These particles were found to have the e/m value as $+9.579 \times 10^4$ coulomb/g. This was the maximum value of e/m observed for any positive particle. It was thus assumed that the positive particle given by hydrogen represents a fundamental particle of positive charge. This particle was named **proton** by **Rutherford** in 1911. Its charge was found to be equal in magnitude but opposite in sign to that of electron.

Thus, **proton carries a charge $+1.602 \times 10^{-19}$ coulomb, *i. e.*, one unit positive charge.**

The mass of the proton, thus, can be calculated.

$$\text{Mass of the proton} = \frac{e}{e/m} = \frac{1.602 \times 10^{-19}}{9.579 \times 10^4}$$

$$= 1.672 \times 10^{-24}\ \text{g}$$

or

$$= 1.672 \times 10^{-27}\ \text{kg}$$

$$\text{Mass of the proton in amu} = \frac{1.672 \times 10^{-24}}{1.66 \times 10^{-24}} = 1.0072\ \text{amu}$$

A proton is defined as a subatomic particle which has a mass nearly 1 amu and a charge of +1 unit ($+1.602 \times 10^{-19}$ coulomb).

Protons are produced in a number of nuclear reactions. On the basis of such reactions, proton has been recognised as a fundamental building unit of the atom.

2.4 RUTHERFORD EXPERIMENT—DISCOVERY OF NUCLEUS

After the discovery of electron and proton, the question arose how these charged particles are distributed in an atom. The answer was given by J.J. Thomson in the form of first model of the atom.

He proposed that the positive charge is spread over a sphere in which the electrons are embedded to make the atom as a whole neutral. This model was much like raisins in a pudding and is also known as *Thomson's plum pudding model.* This model was discarded as it was not consistent with the results of further investigations such as scattering of α-particles by thin metal foils.

In 1911, Ernest Rutherford and his co-workers carried out a series of experiments using α-particles* (Fig. 2.3 and 2.4). A beam of α-particles was directed against a thin foil of about 0.0004 cm thickness of gold, platinum, silver or copper

*The radiations emitted by radioactive substances consist of α-particles. These particles are positively charged. These particles are actually helium atoms from which electrons have been removed. Each α-particle consists of a mass equal to about 4 times that of hydrogen atom and carries a positive charge of two units. It is represented by the symbol α or ${}^4_2\text{He}$.

$$\underset{\text{Helium atom}}{\text{He}} \longrightarrow \underset{\alpha\text{-particle}}{\text{He}^{2+}} + \underset{\text{Electron}}{2e}$$

α-particles are usually obtained from a natural isotope of polonium-214.

respectively. The foil was surrounded by a circular fluorescent zinc sulphide screen. Whenever an α-particle struck the screen, it produced a flash of light.

The following observations were made:

(i) Most of the α-particles (nearly 99%) went straight without suffering any deflection.

(ii) A few of them got deflected through small angles.

(iii) A very few (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even came back in more or less the direction from which they have come, *i.e.*, a deflection of 180°.

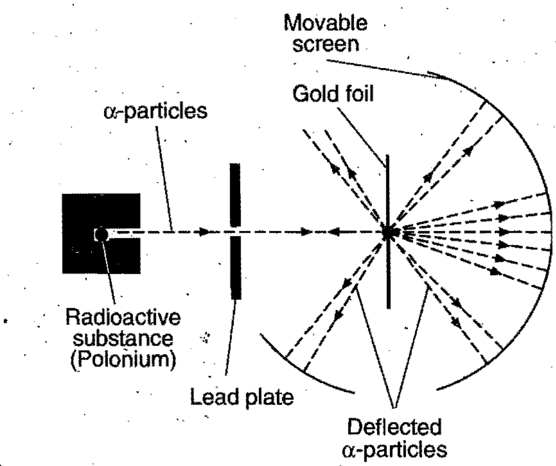


Fig. 2.3

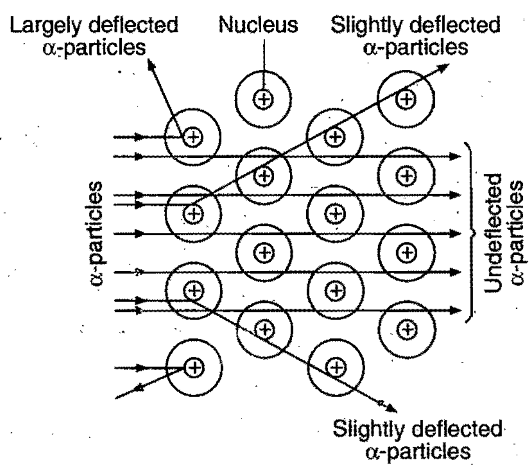


Fig. 2.4 (a)

Consider an α-particle of mass 'm' moving directly towards a nucleus with velocity 'v' at any given time. As this α-particle approaches the nucleus, its velocity and hence kinetic energy continues to decrease. At a certain distance r_0 from the nucleus, the α-particle will stop and then start retracing its depicted path. This distance is called the distance of closest approach. At this distance, the kinetic energy of the α-particle is transformed into electrostatic potential energy. If Z be the atomic number of the nucleus, then

$$\frac{1}{2}mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{Z_e \times 2e}{r_0}$$

$$\because \text{ Electrostatic PE} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r}$$

$$r_0 = \frac{1}{4\pi\varepsilon_0}\frac{4Ze^2}{mv^2}$$

$$r_0 = \frac{1}{4\pi\varepsilon_0}\frac{2Ze^2}{E_K}$$

where, E_K is the original kinetic energy of the α-particles.

Here, $$\frac{1}{4\pi\varepsilon_0} = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2} \text{ (MKS)}$$
$$= 1 \text{(CGS)}$$

The distance of closest approach is of the order of 10^{-14} m. So, the radius of the nucleus should be less than 10^{-14} m.

Following conclusions were drawn from the above observations:

(i) Since, most of the α-particles went straight through the metal foil undeflected, it means that **there must be very large empty space within the atom** or **the atom is extraordinarily hollow.**

(ii) A few of the α-particles were deflected from their original paths through moderate angles; it was concluded that whole of the positive charge is concentrated and the space occupied by this positive charge is very small in the atom. When α-particles come closer to this point, they suffer a force of repulsion and deviate from their paths.

The positively charged heavy mass which occupies only a small volume in an atom is called **nucleus.** It is supposed to be present at the centre of the atom.

(iii) A very few of the α-particles suffered strong deflections or even returned on their path indicating that the nucleus is rigid and α-particles recoil due to direct collision with the heavy positively charged mass.

The graph between angle of scattering and the number of α-particles scattering in the corresponding direction is as shown in Fig. 2.4 (b).

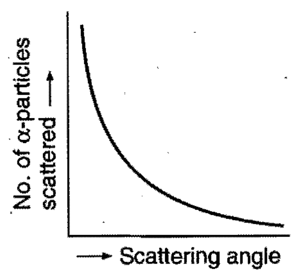


Fig. 2.4 (b)

Information of Rutherford's scattering equation can be memorised by the following relations:

(a) Kinetic energy of α-particles:
$$N = K_1 / [(1/2)mv^2]^2$$

(b) Scattering angle 'θ':
$$N = K_2 / [\sin^4 (\theta/2)]$$

(c) Nuclear charge:
$$N = K_3 (Ze)^2$$

Here, N = Number of α-particles striking the screen and K_1, K_2 and K_3 are the constants.

2.5 MOSELEY EXPERIMENT—ATOMIC NUMBER

Roentgen, in 1895, discovered that when high energy electrons in a discharge tube collide with the anode, penetrating radiations are produced which he named X-rays (Fig. 2.5).

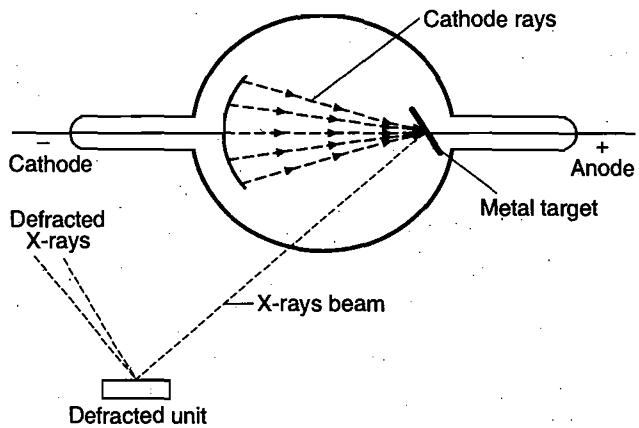


Fig. 2.5

X-rays are electromagnetic radiations of very small wavelengths (0.1–20 Å). X-rays are diffracted by diffraction gratings like ordinary light rays and X-ray spectra are, thus, produced. Each such spectrum is a characteristic property of the element used as anode.

Moseley (1912–1913), investigated the X-ray spectra of 38 different elements, starting from aluminium and ending in gold. He measured the frequency of principal lines of a particular series (the α-lines in the K series) of the spectra. It was observed that the frequency of a particular spectral line gradually increased with the increase of atomic mass of the element. But, it was soon realised that the frequency of the particular spectral line was more precisely related with the serial number of the element in the periodic table which he termed as atomic number (Z). He presented the following relationship:

$$\sqrt{\nu} = a(Z - b)$$

where, ν = frequency of X-rays, Z = atomic number, a and b are constants. When the values of square root of the frequency were plotted against atomic numbers of the elements producing X-rays, a straight line was obtained (Fig. 2.6).

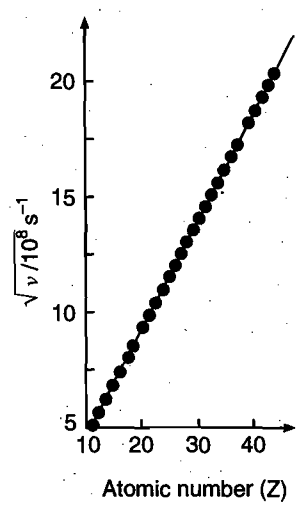


Fig. 2.6

van den Broek (1913) pointed out that the atomic number of an element is equal to the total positive charge contained in the nucleus of its atom. Rutherford was also having the same opinion that the atomic number of an element represents the number of protons in the nucleus of its atom. Thus,

Atomic number of the element
= Serial number of the element in periodic table
= Charge on the nucleus of the atom of the element
= Number of protons present in the nucleus of the atom of the element
= Number of extranuclear electrons present in the atom of the element

2.6 DISCOVERY OF NEUTRON

The discovery of neutron was actually made about 20 years after the structure of atom was elucidated by Rutherford. Atomic masses of different atoms could not be explained if it was accepted that atoms consisted only of protons and electrons. Thus, Rutherford (1920) suggested that in an atom, there must be present at least a third type of fundamental particles which should be electrically neutral and possess mass nearly equal to that of proton. He proposed the name for such fundamental particle as **neutron.** In 1932, **Chadwick** bombarded beryllium with a stream of α-particles. He observed that penetrating radiations were produced which were not affected by electric and magnetic fields. These radiations consisted of neutral particles, which were called neutrons. The nuclear reaction can be shown as:

$$\underset{\text{Beryllium}}{{}^{9}_{4}\text{Be}} + \underset{\alpha\text{-particle}}{{}^{4}_{2}\text{He}} \longrightarrow \underset{\text{Carbon}}{{}^{12}_{6}\text{C}} + \underset{\text{Neutron}}{{}^{1}_{0}n}$$

The mass of the neutron was determined. It was 1.675×10^{-24} g, *i.e.*, nearly equal to the mass of proton.

Thus, **a neutron is a subatomic particle which has a mass 1.675×10^{-24} g, approximately 1 amu, or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge.** The e/m value of a neutron is thus zero.

2.7 RUTHERFORD MODEL

On the basis of scattering experiments, Rutherford proposed a model of the atom which is known as nuclear atomic model. According to this model:

(i) An atom consists of a heavy positively charged nucleus where all the protons and neutrons are present. Protons and neutrons are collectively referred to as **nucleons.** Almost whole of the mass of the atom is contributed by these nucleons. The magnitude of the positive charge on the nucleus is different for different atoms.

(ii) The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.

$$\frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^{5}$$

Thus, diameter (size) of an atom is 100,000 times the diameter of the nucleus.*

The radius of a nucleus is proportional to the cube root of the number of nucleons within it.

$$R = R_0 A^{1/3} \text{ cm}$$

where, $R_0 = 1.33 \times 10^{-13}$ cm; A = mass number; R = Radius of the nucleus.

Rutherford and **Marsden** calculated the density of the hydrogen nucleus containing only one proton.

$$d = \frac{\text{Mass}}{\text{Volume}} = \frac{[A \times 1.66 \times 10^{-24} \text{ g}]}{\frac{4}{3} \times \pi R^3 \text{ cm}^3}$$

$$= \frac{A \times 1.66 \times 10^{-24}}{\frac{4}{3} \times 3.14 \times (1.33 \times 10^{-13})^3 \times A}$$

$$= 1.685 \times 10^{14} \text{ g/cm}^3$$

(iii) There is an empty space around the nucleus called extranuclear part. In this part, electrons are present. The number of electrons in an atom is always equal to number of protons present in the nucleus. As the nucleus part of the atom is responsible for the mass of the atom, the extranuclear part is responsible for its volume. The volume of an atom is about 10^{15} times the volume of the nucleus.

$$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = \frac{10^{-24}}{10^{-39}} = 10^{15}$$

(iv) Electrons revolve round the nucleus in closed orbits with high speed. The centrifugal force acting on the revolving electrons is being counterbalanced by the force of attraction between the electrons and the nucleus.

This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets. The electrons are, therefore, generally referred to as **planetary electrons.**

Dissimilarities between Nuclear Atomic Model and Solar System

(i) The sun and the planets are very big bodies and uncharged while the nucleus and electrons are very small objects and charged.

(ii) The revolution of the planets in the solar system is governed by gravitational forces, while the revolution of electrons around the nucleus is governed by electrostatic forces.

(iii) In the solar system, there is only one planet which revolves in any particular orbit, but in the nuclear atomic model more than one electron may rotate in any particular orbit.

Drawbacks of Rutherford Model

(i) According to classical electromagnetic theory, when a charged particle moves under the influence of attractive force, it loses energy continuously in the form of electromagnetic radiations. Thus, when the electron (a charged particle) moves in an attractive field (created by protons present in the nucleus), it must emit radiations. As a result of this, the electron should lose energy at every turn and move closer and closer to the nucleus following a spiral path (Fig. 2.7). The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable. Bohr made calculations and pointed out that an atom would collapse in 10^{-8} seconds. Since, the atom is quite stable, it means the electrons do not fall into the nucleus, thereby this model does not explain the stability of the atom.

(ii) If the electrons lose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies. Hence, the loss of energy by the electrons is not continuous in an atom.

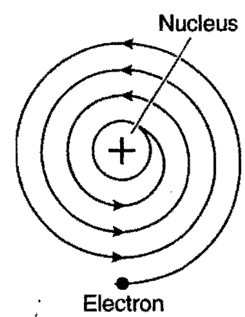


Fig. 2.7

2.8 ELECTROMAGNETIC RADIATIONS

These are energy radiations which do not need any medium for propagation, *e.g.*, visible, ultraviolet, infrared, X-rays, γ-rays, etc. An electromagnetic radiation is generated by oscillations of a charged body in a magnetic field or a magnet in an electrical field. The frequency of a wave is the frequency of oscillation of the oscillating charged particle. These radiations or waves have electrical and magnetic fields associated with them and travel at right angle to these fields. The following are thus the important characteristics of electromagnetic radiations:

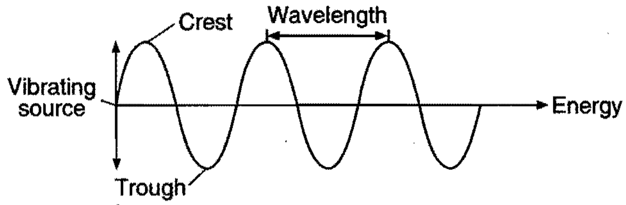
- All electromagnetic radiations travel with the velocity of light.
- These consist of electric and magnetic fields that oscillate in directions perpendicular to each other and perpendicular to the direction in which the wave is travelling.

S. No.	Name	Wavelength (Å)	Frequency (Hz)	Source
1.	Radio wave	$3 \times 10^{14} - 3 \times 10^7$	$1 \times 10^5 - 1 \times 10^9$	Alternating current of high frequency
2.	Micro wave	$3 \times 10^7 - 6 \times 10^6$	$1 \times 10^9 - 5 \times 10^{11}$	Klystron tube
3.	Infrared (IR)	$6 \times 10^6 - 7600$	$5 \times 10^{11} - 3.95 \times 10^{16}$	Incandescent objects
4.	Visible	7600–3800	$3.95 \times 10^{16} - 7.9 \times 10^{14}$	Electric bulbs, sun rays
5.	Ultraviolet (UV)	3800–150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, arc lamps with mercury vapours
6.	X-Rays	150–0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate
7.	γ-Rays	0.1–0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Secondary effect of radioactive decay
8.	Cosmic rays	0.01–Zero	3×10^{20}–Infinity	Outer space

*The diameter of various atoms lies in the range of 0.74 to 4.70 Å (1 Å = 10^{-8} cm).

A wave is always characterized by the following six characteristics:

(i) Wavelength: The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ (lambda) and is measured in terms of centimetre (cm), angstrom (Å), micrometre (μm) or nanometre (nm).



$$1\,\text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m}$$
$$1\ \mu\text{m} = 10^{-4}\ \text{cm} = 10^{-6}\ \text{m}$$
$$1\ \text{nm} = 10^{-7}\ \text{cm} = 10^{-9}\ \text{m}$$
$$1\ \text{cm} = 10^{8}\ \text{Å} = 10^{4}\ \mu\text{m} = 10^{7}\ \text{nm}$$

(ii) Frequency: It is defined as the number of waves which pass through a point in one second. It is denoted by the symbol ν (nu) and is measured in terms of cycles (or waves) per second (cps) or hertz (Hz).

$$\lambda\nu = \text{distance travelled in one second}$$
$$= \text{velocity} = c$$

or $$\nu = \frac{c}{\lambda}$$

(iii) Velocity: It is defined as the distance covered in one second by the wave. It is denoted by the letter 'c'. All electromagnetic waves travel with the same velocity, *i.e.*, 3×10^{10} cm/sec.

$$\lambda\nu = 3 \times 10^{10}$$

Thus, a wave of higher frequency has a shorter wavelength while a wave of lower frequency has a longer wavelength.

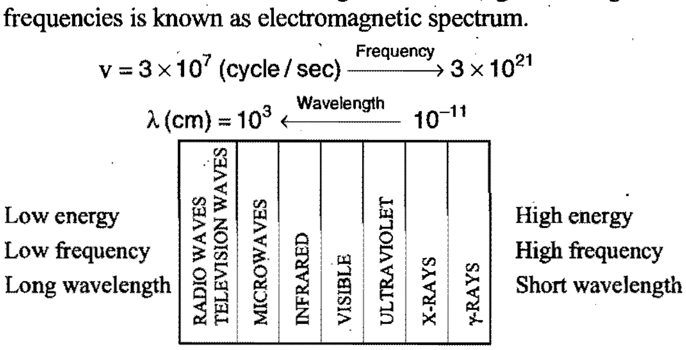
(iv) Wave number: This is the reciprocal of wavelength, *i.e.*, the number of wavelengths per centimetre. It is denoted by the symbol $\bar{\nu}$ (nu bar).

$$\bar{\nu} = \frac{1}{\lambda}$$

It is expressed in cm^{-1} or m^{-1}.

(v) Amplitude: It is defined as the height of the crest or depth of the trough of a wave. It is denoted by the letter 'a'. It determines the intensity of the radiation.

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelengths or frequencies is known as electromagnetic spectrum.



(vi) Time period: Time taken by the wave for one complete cycle or vibration is called time period. It is denoted by T.

$$T = \frac{1}{\nu}$$

Unit: Second per cycle.

2.9 EMISSION SPECTRA—HYDROGEN SPECTRUM

Spectrum is the impression produced on a screen when radiations of particular wavelengths are analysed through a prism or diffraction grating. It is broadly of two types:

(i) Emission spectra (ii) Absorption spectra.

Difference between Emission and Absorption Spectrum

Emission spectrum	Absorption spectrum
1. It gives bright lines (coloured) on the dark background.	It gives dark lines on the bright background.
2. Radiations from emitting source are analysed by the spectroscope.	It is observed when the white light is passed through the substance and the transmitted radiations are analysed by the spectroscope.
3. It may be continuous (if source emits white light) and may be discontinuous (if the source emits coloured light).	These are always discontinuous.

Emission spectra: It is obtained from the substances which emit light on excitation, *i.e.*, either by heating the substances on a flame or by passing electric discharge through gases at low pressure or by passing electric current discharge through a thin filament of a high melting point metal. Emission spectra are of two types:

(a) Continuous spectra and (b) Discontinuous spectra.

(a) Continuous spectra: When white light is allowed to pass through a prism, it gets resolved into several colours (Fig. 2.8). The spectrum is a rainbow of colours, *i.e.*, violet merges into blue, blue into green, and so on. This is a continuous spectrum.

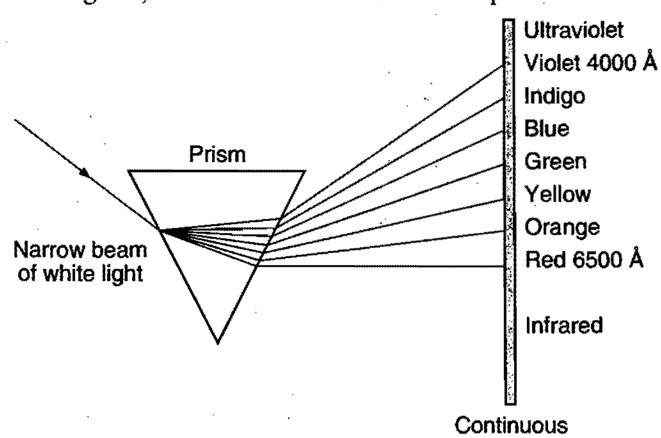


Fig. 2.8 Continuous spectrum of white light

(b) Discontinuous spectra: When gases or vapours of a chemical substance are heated in an electric arc or in a Bunsen flame, light is emitted. If a ray of this light is passed through a prism, a line spectrum is produced. This spectrum consists of a limited number of lines, each of which corresponds to a different wavelength of light. The line spectrum of each element is unique. Hydrogen spectrum is an example of line emission spectrum or atomic emission spectrum.

When an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted. When a ray of this light is passed through a prism, a discontinuous line spectrum of several isolated sharp lines is obtained. The wavelengths of various lines show that these lines lie in visible, ultraviolet and infrared regions. All these lines observed in the hydrogen spectrum can be classified into six series.

Spectral series	Discovered by	Appearing in
Lyman series	Lyman	Ultraviolet region
Balmer series	Balmer	Visible region
Paschen series	Paschen	Infrared region
Brackett series	Brackett	Infrared region
Pfund series	Pfund	Infrared region
Humphrey series	Humphrey	Far infrared region

Ritz presented a mathematical formula to find the wavelengths of various hydrogen lines.

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where, R is a universal constant, known as Rydberg constant. Its value is 109,678 cm^{-1}, n_1 and n_2 are integers (such that $n_2 > n_1$). For a given spectral series, n_1 remains constant while n_2 varies from line to line in the same series.

The value of $n_1 = 1, 2, 3, 4$ and 5 for the Lyman, Balmer, Paschen, Brackett and Pfund series respectively. n_2 is greater than n_1 by at least 1.

Values of n_1 and n_2 for various series

Spectral series	Value of n_1	Value of n_2
Lyman series	1	2, 3, 4, 5, ...
Balmer series	2	3, 4, 5, 6, ...
Paschen series	3	4, 5, 6, 7, ...
Brackett series	4	5, 6, 7, 8, ...
Pfund series	5	6, 7, 8, 9, ...

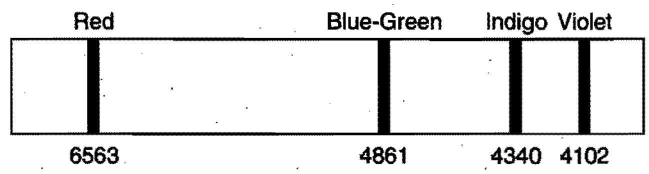


Fig. 2.9 (a) Balmer series in the hydrogen spectrum

Lyman series: $\bar{v} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$

$n_2 = 2, 3, 4, 5, \ldots$

Obtained in emission as well as in absorption spectrum ratio of m^{th} to n^{th} wavelength of Lyman series.

$$\frac{\lambda_m}{\lambda_n} = \left(\frac{m+1}{n+1}\right)^2 \cdot \left\{\frac{(n+1)^2 - 1}{(m+1)^2 - 1}\right\}$$

Balmer series: $\bar{v} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$

$n_2 = 3, 4, 5, 6, \ldots$

Obtained only in emission spectrum.

Paschen series: $\bar{v} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right]$

$n_2 = 4, 5, 6, 7, \ldots$

Brackett series: $\bar{v} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right]$

$n_2 = 5, 6, 7, 8, \ldots$

Pfund series: $\bar{v} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{5^2} - \frac{1}{n_2^2}\right]$

$n_2 = 6, 7, 8, 9, \ldots$

Note : (i) Atoms give line spectra while molecules give band spectra.
(ii) Balmer, Paschen, Brackett, Pfund series are found in emission spectrum.

Electronic transition	Name of line	Wave no.	Wavelength and colour
$\underset{(M)}{n_2 = 3} \longrightarrow \underset{(L)}{n_1 = 2}$	H_α (First line)	$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5R}{36}$	$\lambda = 6563$ Å (Red)
$\underset{(N)}{n_2 = 4} \longrightarrow \underset{(L)}{n_1 = 2}$	H_β (Second line)	$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \frac{3R}{16}$	$\lambda = 4861$ Å (Blue-Green)
$\underset{(O)}{n_2 = 5} \longrightarrow \underset{(L)}{n_1 = 2}$	H_γ (Third line)	$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{5^2}\right] = \frac{21R}{100}$	$\lambda = 4340$ Å (Indigo)
$\underset{(P)}{n_2 = 6} \longrightarrow \underset{(L)}{n_1 = 2}$	H_δ (Fourth line)	$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{6^2}\right] = \frac{8R}{36}$	$\lambda = 4102$ Å (Violet)

(Above four lines were viewed in Balmer series by naked eye.)

Absorption Spectrum : Suppose the radiations from a continuous source like a hot body (sun light) containing the quanta of all wavelengths passes through a sample of hydrogen gas, then the wavelengths missing in the emergent light give dark lines on the bright background. This type of spectrum that contains lesser number of wavelengths in the emergent light than in incident light is called absorption spectrum.

Let the radiations of wavelengths $\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5$ are passed through the sample of hydrogen gas such that λ_1 and λ_4 are absorbed then the absorption spectrum may be represented as:

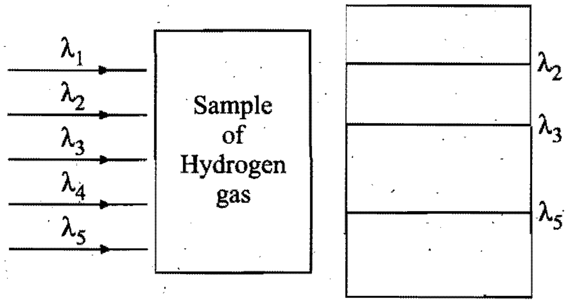


Fig. 2.9 (b) Absorption Spectrum

2.10 QUANTUM THEORY OF RADIATION

The wave theory successfully explains many properties of electromagnetic radiations such as reflection, refraction, diffraction, interference, polarisation, etc., but fails to explain some phenomena like black body radiation, photoelectric effect, etc.

In order to explain black body radiation and photoelectric effect, Max Planck in 1901 presented a new theory which is known as **quantum theory of radiation.** According to this theory, a hot body emits radiant energy not continuously but discontinuously in the form of small packets of energy called **quantum** (in plural quanta). The energy associated with each quantum of a given radiation is proportional to the frequency of the emitted radiation.

$$E \propto \nu$$

Or $E = h\nu$ where, h is a constant known as Planck's constant. Its numerical value is 6.624×10^{-27} erg-sec. The energy emitted or absorbed by a body can be either one quantum or any whole number multiple of $h\nu$, *i.e.*, $2h\nu, 3h\nu, 4h\nu, \ldots, nh\nu$ quanta of energy.

Thus, energy emitted or absorbed = $nh\nu$, where n can have values 1, 2, 3, 4, ... Thus, the energy emitted or absorbed is quantised.

In 1905, Einstein pointed out that light can be supposed to consist of a stream of particles, called **photons.** The energy of each photon of light depends on the frequency of the light, *i.e.*, $E = h\nu$. Energy is also related according to Einstein, as $E = mc^2$ where m is the mass of photon. Thus, it was pointed out that light has wave as well as particle characteristics (dual nature).

SOME SOLVED EXAMPLES

Example 1. *How many protons, electrons and neutrons are present in* 0.18 g $^{30}_{15}P$?

Solution: No. of protons in one atom of P

= No. of electrons in one atom of P = 15

No. of neutrons in one atom of P = $(A - Z) = (30 - 15) = 15$

$$0.18\text{ g } ^{30}_{15}\text{P} = \frac{0.18}{30} = 0.006\text{ mol}$$

No. of atoms in 0.006 mol = $0.006 \times 6.02 \times 10^{23}$

No. of protons in 0.006 mol $^{30}_{15}$P = $15 \times 0.006 \times 6.02 \times 10^{23}$

$= 5.418 \times 10^{22}$

So, No. of electrons = 5.418×10^{22}

and No. of neutrons = 5.418×10^{22}

Example 2. *Calculate the frequency and wave number of radiation with wavelength* 480 *nm.*

Solution: Given,

$$\lambda = 480\text{ nm} = 480 \times 10^{-9}\text{ m} \qquad [\because 1\text{ nm} = 10^{-9}\text{ m}]$$

$$c = 3 \times 10^8\text{ m/sec}$$

$$\text{Frequency, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8\text{ ms}^{-1}}{480 \times 10^{-9}\text{ m}} = 6.25 \times 10^{14}\text{ s}^{-1}$$

$$= 6.25 \times 10^{14}\text{ Hz}$$

Example 3. *Calculate the energy associated with photon of light having a wavelength* 6000 *Å.* [$h = 6.624 \times 10^{-27}$ *erg-sec.*]

Solution: We know that, $E = h\nu = h \cdot \dfrac{c}{\lambda}$

$h = 6.624 \times 10^{-27}$ erg-sec; $c = 3 \times 10^{10}$ cm/sec;

$\lambda = 6000\text{ Å} = 6000 \times 10^{-8}$ cm

$$\text{So, } E = \frac{(6.624 \times 10^{-27}) \times (3 \times 10^{10})}{6 \times 10^{-5}} = 3.312 \times 10^{-12}\text{ erg.}$$

Example 4. *Which has a higher energy, a photon of violet light with wavelength* 4000 *Å or a photon of red light with wavelength* 7000 *Å?* [$h = 6.62 \times 10^{-34}$ *Js*]

Solution: We know that, $E = h\nu = h \cdot \dfrac{c}{\lambda}$

Given, $h = 6.62 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms^{-1}

For a photon of violet light,

$$\lambda = 4000\text{ Å} = 4000 \times 10^{-10}\text{ m}$$

$$E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{4 \times 10^{-7}} = 4.96 \times 10^{-19}\text{ J}$$

For a photon of red light,

$$\lambda = 7000\text{ Å} = 7000 \times 10^{-10}\text{ m}$$

$$E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{7000 \times 10^{-10}} = 2.83 \times 10^{-19}\text{ J}$$

Hence, photon of violet light has higher energy than the photon of red light.

Example 5. *What is the ratio between the energies of two radiations one with a wavelength of* 6000 *Å and other with* 2000 *Å?*

Solution: $\lambda_1 = 6000\text{ Å}$ and $\lambda_2 = 2000\text{ Å}$

$$E_1 = h \cdot \frac{c}{\lambda_1} \text{ and } E_2 = h \cdot \frac{c}{\lambda_2}$$

$$\text{Ratio, } \frac{E_1}{E_2} = \frac{h \cdot c}{\lambda_1} \times \frac{\lambda_2}{h \cdot c} = \frac{\lambda_2}{\lambda_1} = \frac{2000}{6000} = \frac{1}{3}$$

$$\text{or } E_2 = 3E_1$$

Example 6. *Calculate the wavelength, wave number and frequency of photon having an energy equal to three electron volt.* ($h = 6.62 \times 10^{-27}$ *erg-sec.*)

Solution: We know that,

$$E = h \cdot \nu$$

$$\nu = \frac{E}{h} \quad (1\,\text{eV} = 1.602 \times 10^{-12}\ \text{erg})$$

$$= \frac{3 \times (1.602 \times 10^{-12})}{6.62 \times 10^{-27}} = 7.26 \times 10^{14}\ \text{s}^{-1} = 7.26 \times 10^{14}\ \text{Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{10}}{7.26 \times 10^{14}} = 4.132 \times 10^{-5}\ \text{cm}$$

$$\overline{\nu} = \frac{1}{\lambda} = \frac{1}{4.132 \times 10^{-5}} = 2.42 \times 10^{4}\ \text{cm}^{-1}$$

Example 7. *Calculate the energy in kilocalorie per mol of the photons of an electromagnetic radiation of wavelength 7600 Å.*

Solution: $\lambda = 7600\,\text{Å} = 7600 \times 10^{-8}$ cm

$$c = 3 \times 10^{10}\ \text{cm s}^{-1}$$

$$\text{Frequency, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{7600 \times 10^{-8}} = 3.947 \times 10^{14}\ \text{s}^{-1}$$

$$\text{Energy of one photon} = h\nu = 6.62 \times 10^{-27} \times 3.947 \times 10^{14} = 2.61 \times 10^{-12}\ \text{erg}$$

$$\text{Energy of one mole of photons} = 2.61 \times 10^{-12} \times 6.02 \times 10^{23} = 15.71 \times 10^{11}\ \text{erg}$$

Energy of one mole of photons in kilocalorie

$$= \frac{15.71 \times 10^{11}}{4.185 \times 10^{10}} [1\,\text{kcal} = 4.185 \times 10^{10}\ \text{erg}]$$

$$= 37.538\ \text{kcal per mol}$$

Example 8. *Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy in kJ mol $^{-1}$, $h = 6.6256 \times 10^{-34}$ Js.* **(IIT 1992)**

Solution: $\lambda = 242\,\text{nm} = 242 \times 10^{-9}$ m

$$c = 3 \times 10^{8}\ \text{ms}^{-1}$$

$$E = h\nu = h \cdot \frac{c}{\lambda} = 6.6256 \times 10^{-34} \times \frac{3 \times 10^{8}}{242 \times 10^{-9}}$$

$$= 0.082 \times 10^{-17}\ \text{J} = 0.082 \times 10^{-20}\ \text{kJ}$$

$$\text{Energy per mole for ionisation} = 0.082 \times 10^{-20} \times 6.02 \times 10^{23} = 493.6\ \text{kJ mol}^{-1}$$

Example 9. *How many photons of light having a wavelength 4000 Å are necessary to provide 1.00 J of energy?*

Solution: Energy of one photon

$$= h\nu = h \cdot \frac{c}{\lambda}$$

$$= \frac{(6.62 \times 10^{-34})(3.0 \times 10^{8})}{4000 \times 10^{-10}}$$

$$= 4.965 \times 10^{-19}\ \text{J}$$

$$\text{Number of photons} = \frac{1.00}{4.965 \times 10^{-19}} = 2.01 \times 10^{18}$$

Example 10. *Find the number of quanta of radiations of frequency 4.67×10^{13} s^{-1}, that must be absorbed in order to melt 5 g of ice. The energy required to melt 1g of ice is 333 J.*

Solution: Energy required to melt 5 g of ice

$$= 5 \times 333 = 1665\ \text{J}$$

Energy associated with one quantum

$$= h\nu = (6.62 \times 10^{-34}) \times (4.67 \times 10^{13})$$

$$= 30.91 \times 10^{-21}\ \text{J}$$

Number of quanta required to melt 5 g of ice

$$= \frac{1665}{30.91 \times 10^{-21}} = 53.8 \times 10^{21}$$

$$= 5.38 \times 10^{22}$$

Example 11. *Calculate the wavelength of the spectral line, when the electron in the hydrogen atom undergoes a transition from the energy level 4 to energy level 2.*

Solution: According to Rydberg equation,

$$\frac{1}{\lambda} = R\left(\frac{1}{x^2} - \frac{1}{y^2}\right)$$

$$R = 109678\ \text{cm}^{-1}; \quad x = 2; \quad y = 4$$

$$\frac{1}{\lambda} = 109678\left[\frac{1}{4} - \frac{1}{16}\right]$$

$$= 109678 \times \frac{3}{16}$$

On solving, $\lambda = 486$ nm

Example 12. *A bulb emits light of wavelength $\lambda = 4500$ Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second?* **(IIT 1995)**

Solution: Energy emitted per second by the bulb

$$= 150 \times \frac{8}{100}\ \text{J}$$

$$\text{Energy of 1 photon} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{4500 \times 10^{-10}}$$

$$= 4.42 \times 10^{-19}\ \text{joule}$$

Let n photons be evolved per second.

$$\therefore \quad n \times 4.42 \times 10^{-19} = 150 \times \frac{8}{100}$$

$$n = 27.2 \times 10^{18}$$

Example 13. *A near ultraviolet photon of 300 nm is absorbed by a gas and then remitted as two photons. One photon is red with wavelength of 760 nm. What would be the wave number of the second photon?*

Solution:

Energy absorbed = Sum of energy of two quanta

$$\frac{hc}{300 \times 10^{-9}} = \frac{hc}{760 \times 10^{-9}} + \frac{hc}{\lambda \times 10^{-9}}$$

On solving, we get,

$$\bar{\nu}\text{ (wave number)} = \frac{1}{\lambda} = 2.02 \times 10^{-3}\ \text{m}^{-1}$$

Example 14. *Calculate the wavelength of the radiation which would cause the photodissociation of chlorine molecule if the Cl—Cl bond energy is 243 kJ mol $^{-1}$.*

Solution: Energy required to break one Cl—Cl bond

$$= \frac{\text{Bond energy per mole}}{\text{Avogadro's number}}$$

$$= \frac{243}{6.023 \times 10^{23}}\ \text{kJ} = \frac{243 \times 10^3}{6.023 \times 10^{23}}\ \text{J}$$

Let the wavelength of the photon to cause rupture of one Cl—Cl bond be λ.

We know that,

$$\lambda = \frac{hc}{E} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{243 \times 10^3}$$

$$= 4.90 \times 10^{-7}\ \text{m} = 490\ \text{nm}$$

Example 15. *How many moles of photon would contain sufficient energy to raise the temperature of 225 g of water 21°C to 96°C? Specific heat of water is 4.18 J g $^{-1}$ K $^{-1}$ and frequency of light radiation used is $2.45 \times 10^9\ s^{-1}$.*

Solution: Energy associated with one mole of photons

$$= N_0 \times h \times \nu$$

$$= 6.02 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.45 \times 10^9$$

$$= 97.727 \times 10^{-2}\ \text{J mol}^{-1}$$

Energy required to raise the temperature of 225 g of water by 75°C $= m \times s \times t$

$$= 225 \times 4.18 \times 75 = 70537.5\ \text{J}$$

Hence, number of moles of photons required

$$= \frac{mst}{N_0 h\nu} = \frac{70537.5}{97.727 \times 10^{-2}} = 7.22 \times 10^4\ \text{mol}$$

Example 16. *During photosynthesis, chlorophyll-a absorbs light of wavelength 440 nm and emits light of wavelength 670 nm. What is the energy available for photosynthesis from the absorption-emission of a mole of photons?*

Solution:

$$\Delta E = \left[\frac{Nhc}{\lambda}\right]_{\text{absorbed}} - \left[\frac{Nhc}{\lambda}\right]_{\text{evolved}}$$

$$= Nhc\left[\frac{1}{\lambda_{\text{absorbed}}} - \frac{1}{\lambda_{\text{evolved}}}\right]$$

$$= 6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^8 \left[\frac{1}{440 \times 10^{-9}} - \frac{1}{670 \times 10^{-9}}\right]$$

$$= 0.1197[2.272 \times 10^6 - 1.492 \times 10^6]$$

$$= 0.0933 \times 10^6\ \text{J/mol} = 93.3\ \text{kJ/mol}$$

Example 17. *Photochromic sunglasses, which darken when exposed to light, contain a small amount of colourless AgCl (s) embedded in the glass. When irradiated with light, metallic silver atoms are produced and the glass darkens.*

$$AgCl(s) \longrightarrow Ag(s) + Cl$$

Escape of chlorine atoms is prevented by the rigid structure of the glass and the reaction therefore, reverses as soon as the light is removed. If 310 kJ / mol of energy is required to make the reaction proceed, what wavelength of light is necessary?

Solution: Energy per mole = Energy of one Einstein

i.e., energy of one mole quanta

$$= \frac{Nhc}{\lambda}$$

$$\therefore \quad 310 \times 1000 = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$\lambda = 3.862 \times 10^{-7}\ \text{m} = 3862 \times 10^{-10}\ \text{m} = 3862\ \text{Å}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. The frequency of the radiation having wave number 10 m^{-1} is:

(a) 10 s^{-1} (b) 3×10^7 s^{-1}

(c) 3×10^{11} s^{-1} (d) 3×10^9 s^{-1}

[**Ans.** (d)]

[**Hint:** $\bar{\nu} = \frac{1}{\lambda}$

$\nu = c\bar{\nu} = \frac{c}{\lambda} = 3 \times 10^8 \times 10 = 3 \times 10^9\ \text{s}^{-1}$]

2. The energy of a photon of radiation having wavelength 300 nm is:

(a) 6.63×10^{-29} J (b) 6.63×10^{-19} J

(c) 6.63×10^{-28} J (d) 6.63×10^{-17} J

[**Ans.** (b)]

[**Hint:** $E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9}} = 6.63 \times 10^{-19}$ J]

3. The maximum kinetic energy of the photoelectrons is found to be 6.63×10^{-19} J, when the metal is irradiated with a radiation of frequency 2×10^{15} Hz. The threshold frequency of the metal is about:

(a) 1×10^{15} s^{-1} (b) 2×10^{15} s^{-1}

(c) 3×10^{15} s^{-1} (d) 1.5×10^{15} s^{-1}

[**Ans.** (a)]

[**Hint:** $\text{KE} = h(\nu - \nu_0)$

$\nu_0 = \nu - \frac{\text{KE}}{h}$

$= 2 \times 10^{15} - \frac{6.63 \times 10^{-19}}{6.63 \times 10^{-34}} = 1 \times 10^{15}\ \text{s}^{-1}$]

4. The number of photons of light having wavelength 100 nm which can provide 1 J energy is nearly:

(a) 10^7 photons (b) 5×10^{18} photons

(c) 5×10^{17} photons (d) 5×10^7 photons

[**Ans.** (c)]

[**Hint:** $E = \frac{nhc}{\lambda}$

$n = \frac{E\lambda}{hc} = \frac{1 \times 100 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 5 \times 10^{17}$]

5. The atomic transition gives rise to the radiation of frequency (10^4 MHz). The change in energy per mole of atoms taking place would be:

(a) 3.99×10^{-6} J (b) 3.99 J

(c) 6.62×10^{-24} J (d) 6.62×10^{-30} J

[**Ans.** (b)]

[**Hint:** $E = Nh\nu$

$= 6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 10^4 \times 10^6$

$= 3.99$ J]

2.11 BOHR'S ATOMIC MODEL

To overcome the objections of Rutherford's model and to explain the hydrogen spectrum, **Bohr** proposed a **quantum mechanical model** of the atom. This model was based on the quantum theory of radiation and the classical laws of physics. The important postulates on which Bohr's model is based are the following:

(i) The atom has a nucleus where all the protons and neutrons are present. The size of the nucleus is very small. It is present at the centre of the atom.

(ii) Negatively charged electrons are revolving around the nucleus in the same way as the planets are revolving around the sun. The path of the electron is circular. The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

Force of attraction towards nucleus = centrifugal force

(iii) Out of infinite number of possible circular orbits around the nucleus, the electron can revolve only on those orbits whose angular momentum* is an integral multiple of $\frac{h}{2\pi}$, *i.e.*,

$mvr = n\frac{h}{2\pi}$ where m = mass of the electron, v = velocity of electron, r = radius of the orbit and $n = 1, 2, 3, \ldots$ number of the orbit. The angular momentum can have values such as, $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$, etc., but it cannot have a fractional value. Thus, the angular momentum is quantized. The specified or circular orbits (quantized) are called **stationary orbits.**

(iv) By the time, the electron remains in any one of the stationary orbits, it does not lose energy. Such a state is called **ground or normal state.**

In the ground state, potential energy of electron will be minimum, hence it will be the most stable state.

(v) Each stationary orbit is associated with a definite amount of energy. The greater is the distance of the orbit from the nucleus, more shall be the energy associated with it. These orbits are also called energy levels and are numbered as 1, 2, 3, 4, . . . or K, L, M, N, . . . from nucleus outwards.

i.e., $E_1 < E_2 < E_3 < E_4 \ldots$

$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) \ldots$

(vi) The emission or absorption of energy in the form of radiation can only occur when an electron jumps from one stationary orbit to another.

$$\Delta E = E_{\text{high}} - E_{\text{low}} = h\nu$$

Energy is absorbed when the electron jumps from inner to outer orbit and is emitted when it moves from outer to an inner orbit.

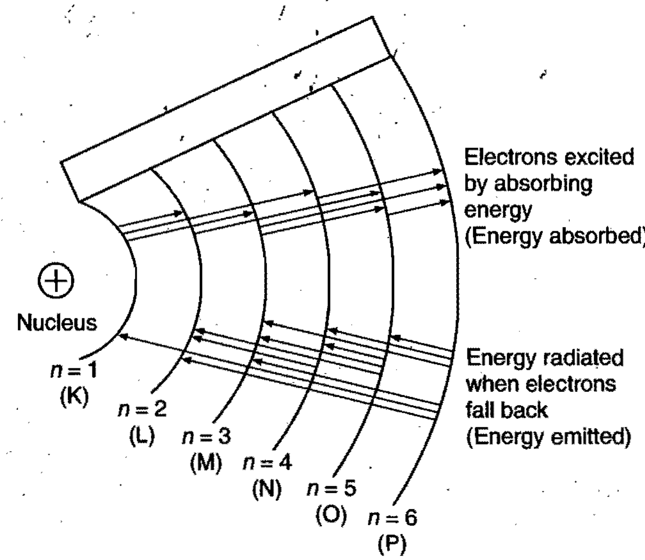


Fig. 2.10

When the electron moves from inner to outer orbit by absorbing definite amount of energy, the new state of the electron is said to be **excited state** (Fig. 2.10).

Using the above postulates, Bohr calculated the radii of various stationary orbits, the energy associated with each orbit and explained the spectrum of hydrogen atom.

Radii of various orbits: Consider an electron of mass 'm' and charge 'e' revolving around the nucleus of charge Ze (Z = atomic number). Let 'v' be the tangential velocity of the revolving electron and 'r' the radius of the orbit (Fig. 2.11). The electrostatic force of attraction between the nucleus and electron (applying Coulomb's law) $= \frac{kZe \times e}{r^2} = \frac{kZe^2}{r^2}$

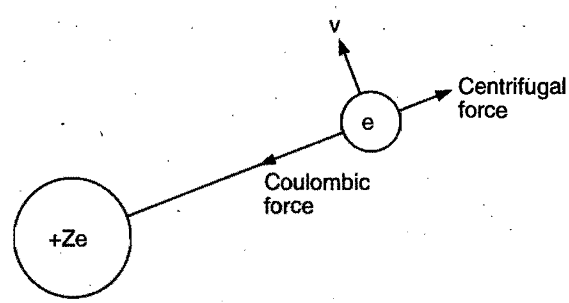


Fig. 2.11

*Angular momentum = $I\omega$, where, I = moment of inertia and ω = angular velocity;
$\omega = \frac{v}{r}$, where, v = linear velocity and r = radius; and $I = mr^2$. So angular momentum $= mr^2 \cdot \frac{v}{r} = mvr$.

where, k is a constant. It is equal to $\frac{1}{4\pi\varepsilon_0}$, ε_0 being absolute permittivity of medium. In SI units, the numerical value of $\frac{1}{4\pi\varepsilon_0}$ is equal to $9\times10^9\ Nm^2/C^2$.

[**Note:** In CGS units, value of k is equal to 1.]

As force of attraction = centrifugal force

So, $$\frac{kZe^2}{r^2}=\frac{mv^2}{r} \quad \text{or} \quad v^2=\frac{kZe^2}{rm}$$

$$v^2=\frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{rm} \quad \ldots \text{(i)}$$

According to one of the postulates,

Angular momentum $= mvr = n\frac{h}{2\pi}$

or $$v=\frac{nh}{2\pi mr} \quad \ldots \text{(ii)}$$

Putting the value of 'v' in eq. (i),

$$\frac{n^2h^2}{4\pi^2m^2r^2}=\frac{kZe^2}{mr} \quad \text{or} \quad \frac{n^2h^2}{4\pi^2mr}=kZe^2$$

or $$r=\frac{n^2h^2}{4\pi^2mkZe^2} \quad \ldots \text{(iii)}$$

Greater is the value of 'n', larger is the size of atom. On the other hand, greater is the value of 'Z', smaller is the size of the atom. Across a period from left to right, atomic number 'Z' increases with constant value of 'n' hence atomic radius decreases towards right. On moving down the group, both 'Z' and 'n' increase but due to shielding, Z^* (effective nuclear charge) remains same. Hence, on moving downwards, atomic radius increases due to increase in 'n'.

For hydrogen atom, $Z = 1$; so $r=\frac{n^2h^2}{4\pi^2mke^2}$

Now putting the values of h, π, m, e and k,

$$r=\frac{n^2\times(6.625\times10^{-34})^2}{4\times(3.14)^2\times(9.1\times10^{-31})\times(1.6\times10^{-19})^2\times(9\times10^9)}$$

$$=0.529\times n^2\times10^{-10}\ \text{m}=0.529\times n^2\ \text{Å}$$

$$=0.529\times10^{-8}\times n^2\ \text{cm}$$

where $h=6.625\times10^{-34}$ J-sec, $\pi = 3.14$

$m=9.1\times10^{-31}$ kg, $e=1.6\times10^{-19}$ coulomb

$k=9\times10^9\ Nm^2/C^2$

Thus, radius of 1st orbit

$$=0.529\times10^{-8}\times1^2=0.529\times10^{-8}\ \text{cm}=0.529\times10^{-10}\ \text{m}$$

Radius of 2nd orbit

$$=0.529\times10^{-8}\times2^2=2.11\times10^{-8}\ \text{cm}=2.11\times10^{-10}\ \text{m}$$

Radius of 3rd orbit

$$=0.529\times10^{-8}\times3^2=4.76\times10^{-8}\ \text{cm}=4.76\times10^{-10}\ \text{m}$$

and so on.

$$r_n=r_1\times n^2 \text{ for hydrogen atom}$$

and $$r_n=0.529\times\frac{n^2}{Z}\ \text{Å} \quad \text{(for hydrogen like species)}$$

Energy of an electron: Let the total energy of the electron be E. It is the sum of kinetic energy and potential energy.

$$E = \text{kinetic energy} + \text{potential energy}$$

$$=\frac{1}{2}mv^2-\frac{kZe^2}{r}$$

Putting the value of mv^2 from eq. (i),

$$E=\frac{kZe^2}{2r}-\frac{kZe^2}{r}=-\frac{kZe^2}{2r}$$

Putting the value of r from eq. (iii),

$$E=-\frac{kZe^2}{2}\times\frac{4\pi^2mkZe^2}{n^2h^2}=-\frac{2\pi^2Z^2k^2me^4}{n^2h^2} \quad \ldots\text{(iv)}$$

For hydrogen atom, $Z = 1$

So, $$E=-\frac{2\pi^2k^2me^4}{n^2h^2}$$

Putting the values of π, k, m, e and h,

$$E=-\frac{2\times(3.14)^2\times(9\times10^9)^2\times(9.1\times10^{-31})\times(1.6\times10^{-19})^4}{n^2\times(6.625\times10^{-34})^2}$$

$$=-\frac{21.79\times10^{-19}}{n^2}\ \text{J per atom}$$

$$E=-\frac{R_H}{n^2} \quad \text{(where, } R_H=2.18\times10^{-18}\ \text{J)}$$

$$=-\frac{13.6}{n^2}\ \text{eV per atom} \quad (1\ \text{J}=6.2419\times10^{18}\ \text{eV})$$

$$=-\frac{313.6}{n^2}\ \text{kcal/mol} \quad (1\ \text{eV}=23.06\ \text{kcal/mol})$$

$$=-\frac{1312}{n^2}\ \text{kJ/mol}$$

$$\text{Kinetic energy in } n\text{th shell}=\frac{13.6\times Z^2}{n^2}\ \text{eV}$$

$$\text{Potential energy in } n\text{th shell}=\frac{-27.2\times Z^2}{n^2}\ \text{eV}$$

Substituting the values of $n = 1, 2, 3, 4, \ldots$, etc., the energy of electron in various energy shells in hydrogen atom can be calculated.

Energy shell	E (Joule per atom)	E (eV per atom)	E (kcal /mol)
1	-21.79×10^{-19}	−13.6	− 313.6
2	-5.44×10^{-19}	−3.4	−78.4
3	-2.42×10^{-19}	−1.51	−34.84
4	-1.36×10^{-19}	− 0.85	−19.6
—	—	—	—
—	—	—	—
∞	0	0	0

$$E_n=\frac{E_1}{n^2} \quad \text{(for hydrogen atom)}$$

and $$E_n=E_1\times\frac{Z^2}{n^2} \quad \text{(for hydrogen like species)}$$

where, E_1 = energy of hydrogen first orbit.

Since, n can have only integral values, it follows that total energy of the electron is quantised. The negative sign indicates that the electron is under attraction towards nucleus, *i.e.*, it is bound to the nucleus. The electron has minimum energy in the first orbit and its energy increases as n increases, *i.e.*, it becomes less negative. The electron can have a maximum energy value of zero when $n = \infty$. The zero energy means that the electron is no longer bound to the nucleus, *i.e.*, it is not under attraction towards nucleus.

For hydrogen like species such as He^+, Li^{2+}, etc., $E_n = Z^2 \times E_n$ for hydrogen atom.

Velocity of an electron: We know that,

Centrifugal force on electron

= force of attraction between nucleus and electron

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \text{(in CGS units)} \qquad \ldots \text{(i)}$$

The angular momentum of an electron is given as:

$$mvr = nh/2\pi \qquad \ldots \text{(ii)}$$

From eqs. (i) and (ii), we have

$$v\left(\frac{nh}{2\pi}\right) = Ze^2$$

$$v = \frac{Z}{n}\left(\frac{2\pi e^2}{h}\right)$$

$$v = \frac{Z}{n} \times 2.188 \times 10^8 \text{ cm/sec} \qquad \ldots \text{(iii)}$$

$$v = \frac{2.188 \times 10^8}{n} \text{ cm/sec} \quad \text{(For hydrogen, } Z = 1\text{)}$$

$$v_1 = 2.188 \times 10^8 \text{ cm/sec}$$

$$v_2 = \frac{1}{2} \times 2.188 \times 10^8 \text{ cm/sec}$$

$$v_3 = \frac{1}{3} \times 2.188 \times 10^8 \text{ cm/sec}$$

Here, v_1, v_2 and v_3 are the velocities of electron in first, second and third Bohr orbits in hydrogen.

From equation (iii),

$$\frac{v_1}{v_2} = \frac{2}{1} \quad \text{and} \quad \frac{v_3}{v_1} = \frac{1}{3} \text{ and so on.}$$

Orbital frequency: Number of revolutions per second by an electron in a shell is called **orbital frequency**; it may be calculated as,

Number of revolutions per second by an electron in a shell

$$= \frac{\text{Velocity}}{\text{Circumference}} = \frac{v}{2\pi r} = -\frac{E_1}{h}\left(\frac{2}{n^3}\right)$$

$$= \frac{Z^2}{n^3} \times 6.66 \times 10^{15}$$

where, E_1 = Energy of first shell.

Time period of revolution of electron in nth orbit (T_n):

$$T_n = \frac{2\pi r}{v_n} = \frac{n^3}{Z^2} \times 1.5 \times 10^{-16} \text{ sec}$$

Interpretation of hydrogen spectrum: The only electron in the hydrogen atom resides under ordinary conditions on the first orbit. When energy is supplied, the electron moves to higher energy shells depending on the amount of energy absorbed. When this electron returns to any of the lower energy shells, it emits energy. Lyman series is formed when the electron returns to the lowest energy state while Balmer series is formed when the electron returns to second energy shell. Similarly, Paschen, Brackett and Pfund series are formed when electron returns to the third, fourth and fifth energy shells from higher energy shells respectively (Fig. 2.12).

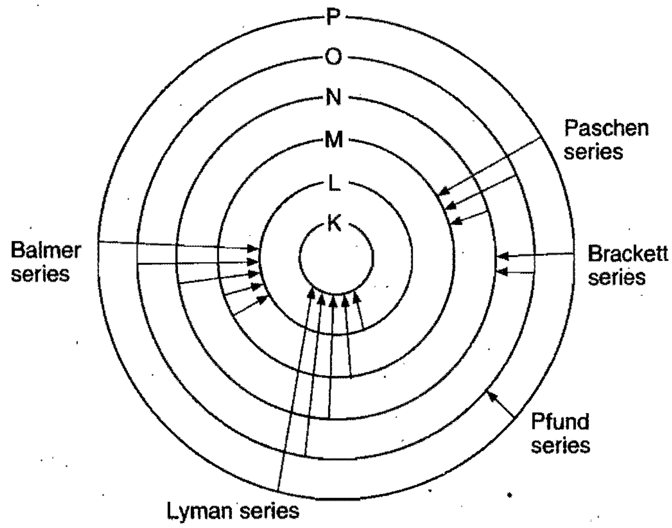


Fig. 2.12

Maximum number of lines produced when an electron jumps from n th level to ground level is equal to $\frac{n(n-1)}{2}$. For example, in the case of $n = 4$, number of lines produced is 6. ($4 \to 3, 4 \to 2, 4 \to 1, 3 \to 2, 3 \to 1, 2 \to 1$). When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will be equal to.

$$\boldsymbol{\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}}$$

If the electron comes back from energy level having energy E_2 to energy level having energy E_1, then the difference may be expressed in terms of energy of photon as:

$$E_2 - E_1 = \Delta E = h\nu$$

or the frequency of the emitted radiation is given by

$$\nu = \frac{\Delta E}{h}$$

Since, ΔE can have only definite values depending on the definite energies of E_2 and E_1, ν will have only fixed values in an atom,

or
$$\nu = \frac{c}{\lambda} = \frac{\Delta E}{h}$$

or
$$\lambda = \frac{hc}{\Delta E}$$

Since, h and c are constants, ΔE corresponds to definite energy; thus, each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom.

Thus, the different spectral lines in the spectra of atoms correspond to different transitions of electrons from higher energy levels to lower energy levels.

Derivation of Rydberg Equation

Let an excited electron from n_2 shell come to the n_1 shell with the release of radiant energy. The wave number $\bar{\nu}$ of the corresponding spectral line may be calculated in the following manner:

$$\Delta E = E_2 - E_1 = (-)\frac{2\pi^2 mZ^2 e^4}{n_2^2 h^2} - (-)\frac{2\pi^2 mZ^2 e^4}{n_1^2 h^2}$$

$$\frac{hc}{\lambda} = \frac{2\pi^2 mZ^2 e^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where, $\Delta E = h\nu = \frac{hc}{\lambda}$

$$\therefore \quad \bar{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 mZ^2 e^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or $\quad \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

where, $\quad R = \frac{2\pi^2 me^4}{ch^3}$ = Rydberg constant = 109743 cm^{-1}

This value of R is in agreement with experimentally determined value 109677.76 cm^{-1}. Rydberg equation for hydrogen may be given as,

$$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Modification of Rydberg Equation

According to the Rydberg equation:

$$\underset{\text{wave number}}{\bar{\nu}} = \frac{2\pi^2 mZ^2 e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

It can be considered that the electron and the nucleus revolve around their common centre of mass. Therefore, instead of the mass of the electron, the reduced mass of the system was introduced and the equation becomes:

$$\bar{\nu} = \frac{2\pi^2 \mu Z^2 e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Reduced mass 'μ' can be calculated as,

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

where, $\quad m$ = mass of electron

and $\quad M$ = mass of nucleus

$$\therefore \quad \mu = \frac{mM}{m+M}$$

(i) *First line of a series:* It is called 'line of longest wavelength' or 'line of shortest energy'.

For first line,

$$n_2 = (n_1 + 1)$$

$$\therefore \quad \bar{\nu}_{\text{first}} = \frac{1}{\lambda_{\text{first}}} = R\left[\frac{1}{n_1^2} - \frac{1}{(n_1+1)^2}\right]$$

Similarly for second, third and fourth lines,

$n_2 = n_1 + 2$; $n_2 = n_1 + 3$ and $n_2 = n_1 + 4$ respectively

$\therefore$ Rydberg equation may be written as,

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{(n_1+x)^2}\right]$$

where, x = number of line in the spectrum.

e.g., $x = 1, 2, 3, 4, \ldots$ for first, second, third and fourth lines in the spectrum respectively.

(ii) *Series limit or last line of a series:* It is the line of shortest wavelength or line of highest energy.

For last line, $\quad n_2 = \infty$

$$\bar{\nu}_{\text{last}} = \frac{1}{\lambda_{\text{last}}} = \frac{R}{n_1^2}$$

Lyman limit $= \frac{R}{1^2}$; Balmer limit $= \frac{R}{2^2}$

Paschen limit $= \frac{R}{3^2}$; Brackett limit $= \frac{R}{4^2}$

Pfund limit $= \frac{R}{5^2}$; Humphrey limit $= \frac{R}{6^2}$

(iii) *Intensities of spectral lines:* The intensities of spectral lines in a particular series decrease with increase in the value of n_2, *i.e.*, higher state.

e.g.,

Lyman series $\underset{(n_2 \to n_1)}{}$ $(2 \to 1) > (3 \to 1) > (4 \to 1) > (5 \to 1)$

Balmer series $\underset{(n_2 \to n_1)}{}$ $(3 \to 2) > (4 \to 2) > (5 \to 2) > (6 \to 2)$

Decreasing intensity of the spectral lines

Ionization Energy and Excitation Energy

$$\text{Excitation potential for } n_1 \to n_2 = \frac{E_{n_2} - E_{n_1}}{\text{Electronic charge}}$$

$$\text{Ionization potential for } n_1 \to \infty = \frac{E_{n_1}}{\text{Electronic charge}}$$

The energy required to remove an electron from the ground state to form cation, *i.e.*, to take the electron to infinity, is called **ionization energy.**

$$\text{IE} = E_\infty - E_{\text{ground}}$$

$$\text{IE} = 0 - E_1(\text{H}) = 13.6\,\text{eV atom}^{-1}$$

$$= 2.17 \times 10^{-18}\ \text{J atom}^{-1}$$

$$\text{IE} = \frac{Z^2}{n^2} \times 13.6\,\text{eV}$$

$$\frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2}$$

$$(\mathrm{IE})_Z = \frac{(\mathrm{IE})_H \times Z^2}{n^2}$$

If an electron is already present in the excited state, then the energy required to remove that electron is called **separation energy.**

$$E_{\text{separation}} = E_{\infty} - E_{\text{excited}}$$

The following points support Bohr theory:

(i) The frequencies of the spectral lines calculated from Bohr equation are in close agreement with the frequencies observed experimentally in hydrogen spectrum.

(ii) The value of Rydberg constant for hydrogen calculated from Bohr equation tallies with that determined experimentally.

(iii) The emission and absorption spectra of hydrogen like species such as He^+, Li^{2+} and Be^{3+} can be explained with the help of Bohr theory.

Limitations of Bohr Theory

(i) It does not explain the spectra of multi-electron atoms.

(ii) When a high resolving power spectroscope is used, it is observed that a spectral line in the hydrogen spectrum is not a simple line but a collection of several lines which are very close to one another. This is known as fine spectrum. Bohr theory does not explain the fine spectra of even the hydrogen atom.

(iii) It does not explain the splitting of spectral lines into a group of finer lines under the influence of magnetic field (Zeeman effect) and electric field (Stark effect).

(iv) Bohr theory is not in agreement with Heisenberg's uncertainty principle.

2.12 SOMMERFELD'S EXTENSION OF BOHR THEORY

To account for the fine spectrum of hydrogen atom, **Sommerfeld,** in 1915, proposed that the moving electron might describe elliptical orbits in addition to circular orbits and the nucleus is situated at one of the foci. During motion on a circle, only the angle of revolution changes while the distance from the nucleus remains the same but in elliptical motion both the angles of revolution and the distance of the electron from the nucleus change. The distance from the nucleus is termed as **radius vector** and the angle of revolution is known as **azimuthal angle.** The tangential velocity of the electron at a particular instant can be resolved into two components: one along the radius vector called

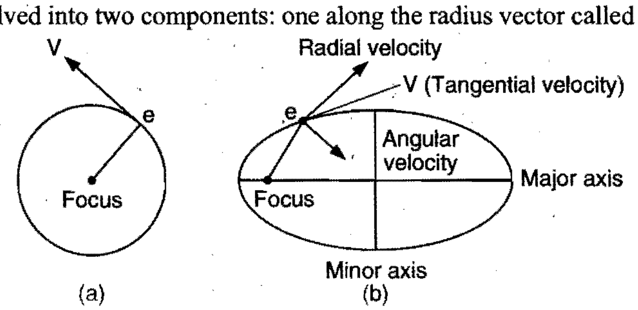


Fig. 2.13

radial velocity and the other perpendicular to the radius vector called **transverse** or **angular velocity.** These two velocities give rise to radial momentum and angular or azimuthal momentum. **Sommerfeld** proposed that both the momenta must be integral multiples of $\frac{h}{2\pi}$ [Fig. 2.13 (b)].

$$\text{Radial momentum} = n_r \frac{h}{2\pi}$$

$$\text{Azimuthal momentum} = n_\phi \frac{h}{2\pi}$$

n_r and n_ϕ are related to the main orbit 'n' as:

$$n = n_r + n_\phi$$

or

$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

(i) 'n_ϕ' cannot be zero because under this condition, the ellipse shall take the shape of a straight line.

(ii) 'n_ϕ' cannot be more than 'n' because minor axis is always smaller than major axis.

(iii) 'n_ϕ' can be equal to 'n'. Under this condition, the major axis becomes equal to minor axis and the ellipse takes the shape of a circle. Thus, n_ϕ can have all integral values up to 'n' but not zero. When the values are less than 'n', orbits are elliptical and when it becomes equal to 'n', the orbit is circular in nature.

For $n = 1$, n_ϕ can have only one value, *i.e.*, 1. Therefore, the first orbit is circular in nature.

For $n = 2$, n_ϕ can have two values 1 and 2, *i.e.*, the second orbit has two sub-orbits, one is elliptical and the other is circular in nature.

For $n = 3$, n_ϕ can have three values 1, 2 and 3, *i.e.*, third orbit has three sub-orbits, two are elliptical and one is circular in nature.

For $n = 4$, n_ϕ can have four values 1, 2, 3 and 4, *i.e.*, fourth orbit has four sub-orbits, three are elliptical and fourth one is circular in nature (Fig. 2.14).

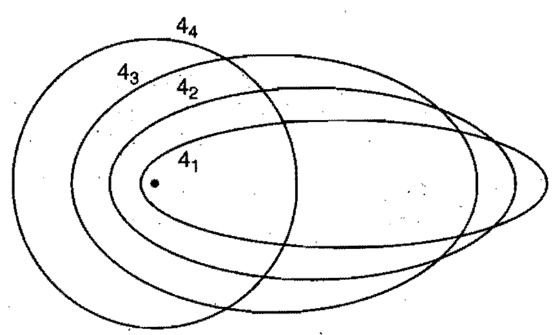


Fig. 2.14

Sommerfeld thus introduced the concept of subenergy shells. In a main energy shell, the energies of subshells differ slightly from one another. Hence, the jumping of an electron from one energy shell to another energy shell will involve slightly different amount of energy as it will depend on subshell also. This explains to some extent the fine spectrum of hydrogen atom. However, Sommerfeld extension fails to explain the spectra of multielectron atoms.

SOME SOLVED EXAMPLES

Example 18. *Calculate the wavelength and energy of radiation emitted for the electronic transition from infinite to stationary state of hydrogen atom. (Given, $R = 1.09678 \times 10^7\ m^{-1}$, $h = 6.6256 \times 10^{-34}$ J-s and $c = 2.9979 \times 10^8\ ms^{-1}$)*

Solution:
$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$n_1 = 1 \text{ and } n_2 = \infty$$
$$\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{(\infty)^2}\right] = R$$
or
$$\lambda = \frac{1}{R} = \frac{1}{1.09678 \times 10^7} = 9.11 \times 10^{-8}\ \text{m}$$

We know that,
$$E = h\nu = h \cdot \frac{c}{\lambda} = 6.6256 \times 10^{-34} \times \frac{2.9979 \times 10^8}{9.11 \times 10^{-8}}$$
$$= 2.17 \times 10^{-18}\ \text{J}$$

Example 19. *Calculate the velocity (cm /sec) of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus.*

Solution: Radius of 3rd orbit
$$= 3^2 \times 0.529 \times 10^{-8} = 4.761 \times 10^{-8}\ \text{cm}$$

We know that,
$$m\upsilon r = \frac{nh}{2\pi} \quad \text{or} \quad \upsilon = \frac{nh}{2\pi mr}$$
$$= \frac{3 \times 6.624 \times 10^{-27}}{2 \times 3.14 \times (9.108 \times 10^{-28}) \times (4.761 \times 10^{-8})}$$
$$= 0.729 \times 10^8\ \text{cm/sec}$$

Time taken for one revolution $= \dfrac{2\pi r}{\upsilon}$

Number of revolutions per second
$$= \frac{1}{\frac{2\pi r}{\upsilon}} = \frac{\upsilon}{2\pi r}$$
$$= \frac{0.729 \times 10^8}{2 \times 3.14 \times 4.761 \times 10^{-8}}$$
$$= 2.4 \times 10^{14}\ \text{revolutions/sec}$$

Example 20. *The electron energy in hydrogen atom is given by $E = -\dfrac{21.7 \times 10^{-12}}{n^2}$ erg. Calculate the energy required to remove an electron completely from $n = 2$ orbit. What is the longest wavelength (in cm) of light that be used to cause this transition?*

Solution:
$$E = -\frac{21.7 \times 10^{-12}}{n^2}\ \text{erg}$$

Electron energy in the 2nd orbit, *i.e.*, $n = 2$,
$$E_2 = -\frac{21.7 \times 10^{-12}}{2^2}\ \text{erg} = -5.425 \times 10^{-12}\ \text{erg}$$

and $E_\infty = 0$

ΔE = Change in energy $= E_\infty - E_2 = 5.425 \times 10^{-12}$ erg

Thus, energy required to remove an electron from 2nd orbit
$$= 5.425 \times 10^{-12}\ \text{erg}$$

According to quantum equation,
$$\Delta E = h \cdot \frac{c}{\lambda}$$
or
$$\lambda = \frac{hc}{\Delta E}$$
$$(h = 6.625 \times 10^{-27}\ \text{erg-sec}; c = 3 \times 10^{10}\ \text{cm/sec})$$
and
$$\Delta E = 5.425 \times 10^{-12}\ \text{erg}$$
So,
$$\lambda = \frac{(6.625 \times 10^{-27}) \times (3 \times 10^{10})}{5.425 \times 10^{-12}}$$
$$= 3.7 \times 10^{-5}\ \text{cm}$$

Thus, the longest wavelength of light that can cause this transition is 3.7×10^{-5} cm.

Example 21. *Calculate the shortest and longest wavelengths in hydrogen spectrum of Lyman series.*

Or

Calculate the wavelengths of the first line and the series limit for the Lyman series for hydrogen. ($R_H = 109678\ cm^{-1}$)

Solution: For Lyman series, $n_1 = 1$.

For shortest wavelength in Lyman series (*i.e.*, series limit), the energy difference in two states showing transition should be maximum, *i.e.*, $n_2 = \infty$.

So,
$$\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = R_H$$
$$\lambda = \frac{1}{109678} = 9.117 \times 10^{-6}\ \text{cm}$$
$$= 911.7\ \text{Å}$$

For longest wavelength in Lyman series (*i.e.*, first line), the energy difference in two states showing transition should be minimum, *i.e.*, $n_2 = 2$

So,
$$\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3}{4}R_H$$
or
$$\lambda = \frac{4}{3} \times \frac{1}{R_H} = \frac{4}{3 \times 109678} = 1215.7 \times 10^{-8}\ \text{cm}$$
$$= 1215.7\ \text{Å}$$

Example 22. *Show that the Balmer series occurs between 3647 Å and 6563 Å. ($R = 1.0968 \times 10^7\ m^{-1}$)*

Solution: For Balmer series,
$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

where, $n = 3, 4, 5, \ldots \infty$

To obtain the limits for Balmer series $n = 3$ and $n = \infty$ respectively.

$$\lambda_{max}\ (n=3) = \frac{1}{R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]} = \frac{36}{5R}$$

$$= \frac{36}{5 \times 1.0968 \times 10^7}\ \text{m}$$

$$= 6563\ \text{Å}$$

$$\lambda_{min}\ (n=\infty) = \frac{1}{R\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right]} = \frac{4}{R}$$

$$= \frac{4}{1.0968 \times 10^7}\ \text{m}$$

$$= 3647\ \text{Å}$$

Example 23. *Light of wavelength 12818 Å is emitted when the electron of a hydrogen atom drops from 5th to 3rd orbit. Find the wavelength of the photon emitted when the electron falls from 3rd to 2nd orbit.*

Solution: We know that,

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

When, $n_1 = 3$ and $n_2 = 5$,

$$\frac{1}{12818} = R\left[\frac{1}{9} - \frac{1}{25}\right] = \frac{16R}{9 \times 25}$$

or $$12818 = \frac{9 \times 25}{16 \times R} \qquad \ldots(i)$$

When, $n_1 = 2$ and $n_2 = 3$,

$$\frac{1}{\lambda} = R\left[\frac{1}{4} - \frac{1}{9}\right] = \frac{5R}{36}$$

$$\lambda = \frac{36}{5R} \qquad \ldots(ii)$$

Dividing eqn. (ii) by eqn. (i),

$$\frac{\lambda}{12818} = \frac{36}{5R} \times \frac{16R}{9 \times 25} = \frac{64}{125}$$

$$\lambda = \frac{64}{125} \times 12818 = 6562.8\ \text{Å}$$

Example 24. *The ionisation energy of hydrogen atom is 13.6 eV. What will be the ionisation energy of He^+ and Li^{2+} ions?*

Solution: Ionisation energy $= -$(energy of the 1st orbit)

Energy of the 1st orbit of hydrogen $= -13.6$ eV

Energy of the 1st orbit of $He^+ = -13.6 \times Z^2$ (Z for $He^+ = 2$)

$= -13.6 \times 4$ eV $= -54.4$ eV

So, Ionisation energy of $He^+ = -(-54.4) = 54.4$ eV

Energy of 1st orbit of $Li^{2+} = -13.6 \times 9$ (Z for $Li^{2+} = 3$)

$= -122.4$ eV

Ionisation energy of $Li^{2+} = -(-122.4) = 122.4$ eV

Example 25. *If the energy difference between two electronic states is 46.12 kcal mol^{-1}, what will be the frequency of the light emitted when the electrons drop from higher to lower states? ($Nh = 9.52 \times 10^{-14}$ kcal sec mol^{-1}, where, N is the Avogadro's number and h is the Planck's constant)*

Solution: $\Delta E = 46.12$ kcal mol^{-1}

According to Bohr theory, $\Delta E = Nh\nu$

or $$\nu = \frac{\Delta E}{Nh} = \frac{46.12}{9.52 \times 10^{-14}}$$

$$= 4.84 \times 10^{14}\ \text{cycle sec}^{-1}$$

Example 26. *According to Bohr theory, the electronic energy of the hydrogen atom in the nth Bohr orbit is given by*

$$E_n = -\frac{21.76 \times 10^{-19}}{n^2}\ J$$

Calculate the longest wavelength of light that will be needed to remove an electron from the 3rd orbit of the He^+ ion.

(IIT 1990)

Solution: The electronic energy of He^+ ion in the nth Bohr orbit

$$= -\frac{21.76 \times 10^{-19}}{n^2} \times Z^2\ \text{J}$$

where, $Z = 2$

Thus, energy of He^+ in the 3rd Bohr orbit

$$= -\frac{21.76 \times 10^{-19}}{9} \times 4\ \text{J}$$

$$\Delta E = E_\infty - E_3$$

$$= 0 - \left[-\frac{21.76 \times 10^{-19} \times 4}{9}\right]$$

$$= \frac{21.76 \times 10^{-19} \times 4}{9}$$

We know that, $$\lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 9}{21.76 \times 10^{-19} \times 4}$$

$$= 2.055 \times 10^{-7}\ \text{m}$$

Example 27. *Calculate the ratio of the velocity of light and the velocity of electron in the first orbit of a hydrogen atom. (Given, $h = 6.624 \times 10^{-27}$ erg-sec; $m = 9.108 \times 10^{-28}$ g, $r = 0.529 \times 10^{-8}$ cm)*

Solution: $$v = \frac{h}{2\pi mr}$$

$$= \frac{6.624 \times 10^{-27}}{2 \times 3.14 \times 9.108 \times 10^{-28} \times 0.529 \times 10^{-8}}$$

$$= 2.189 \times 10^8\ \text{cm/sec}$$

$$\frac{c}{v} = \frac{3 \times 10^{10}}{2.189 \times 10^8} = 137$$

Example 28. *The wavelength of a certain line in Balmer series is observed to be 4341 Å. To what value of 'n' does this correspond? (R_H = 109678 cm^{-1})*

Solution:
$$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$
$$\frac{1}{n^2} = \frac{1}{4} - \frac{1}{\lambda \times R_H}$$
$$= \frac{1}{4} - \frac{1}{4341 \times 10^{-8} \times 109678}$$
$$= 0.04$$
$$n^2 = \frac{1}{0.04} = 25$$
or
$$n = 5$$

Example 29. *Estimate the difference in energy between the first and second Bohr orbit for hydrogen atom. At what minimum atomic number would a transition from n = 2 to n = 1 energy level result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen-like species does this atomic number correspond to?* **(IIT 1993)**

Solution: $\Delta E = h\nu = \dfrac{h \cdot c}{\lambda}$

and
$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\Delta E = R \cdot h \cdot c\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\Delta E = h \cdot c \cdot \frac{3}{4} R$$
$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 1.09678 \times 10^7 \times 3}{4}$$
$$= 1.635 \times 10^{-18} \text{ J}$$

For hydrogen-like species,
$$\Delta E = Z^2 \, Rhc\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\frac{1}{\lambda} = Z^2 R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\frac{1}{3.0 \times 10^{-8}} = Z^2 \times 1.09678 \times 10^7 \times \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$
$$Z^2 = \frac{4}{3 \times 10^{-8} \times 1.09678 \times 10^7 \times 3} \approx 4$$
or
$$Z = 2$$

The species is He^+.

Example 30. *What transition in the hydrogen spectrum have the same wavelength as Balmer transition n = 4 to n = 2 of He^+ spectrum?* **(IIT 1993)**

Solution: For He^+ ion,
$$\frac{1}{\lambda} = Z^2 R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$= (2)^2 R\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \frac{3R}{4}$$

For hydrogen atom,
$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
So,
$$\frac{3R}{4} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
or
$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$
i.e., $n_1 = 1$ and $n_2 = 2$

Example 31. *Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum. ($R_H = 1.1 \times 10^7$ m^{-1}; $c = 3 \times 10^8$ $m s^{-1}$; $h = 6.62 \times 10^{-34}$ J-s)* **(IIT 1993)**

Solution: The transition occurs like Balmer series as spectral line is observed in visible region.

Thus, the line of lowest energy will be observed when transition occurs from 3rd orbit to 2nd orbit, *i.e.*, $n_1 = 2$ and $n_2 = 3$.
$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5}{36} R$$
$$E = h\nu = h \cdot \frac{c}{\lambda} = 6.62 \times 10^{-34} \times 3 \times 10^8 \times \frac{5}{36} \times 1.1 \times 10^7$$
$$= 3.03 \times 10^{-19} \text{ J per atom}$$

Energy corresponding to 1.0 g atom of hydrogen
$$= 3.03 \times 10^{-19} \times \text{Avogadro's number}$$
$$= 3.03 \times 10^{-19} \times 6.023 \times 10^{23} \text{ J}$$
$$= 18.25 \times 10^4 \text{ J}$$

Example 32. *How many times does the electron go around the first Bohr's orbit of hydrogen in one second?*

Solution: Number of revolutions per second $= \dfrac{v}{2\pi r}$ ... (i)
$$v = \frac{2.188 \times 10^8}{n} \text{ cm/sec}$$
$$v = \frac{2.188 \times 10^8}{1} = 2.188 \times 10^8 \text{ cm/sec}$$
$$r = \frac{n^2}{Z} \times 0.529 \text{ Å}$$
$$= \frac{1^2}{1} \times 0.529 \times 10^{-8} \text{ cm}$$
$$= 0.529 \times 10^{-8} \text{ cm}$$

$\therefore$ Number of revolutions per sec $= \dfrac{2.188 \times 10^8}{2 \times 3.14 \times 0.529 \times 10^{-8}}$
$$= 6.59 \times 10^{15}$$

Example 33. *Calculate the wavelength of radiations emitted, produced in a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.*
($R_H = 1.1 \times 10^7\ m^{-1}$) **(IIT 1995)**

Solution: $\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$= 1.1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2}\right)$$

$$= 969.6 \times 10^{-10} \text{ metre}$$

$\therefore$ $\lambda = 969.6\,\text{Å}$

Example 34. *What is the degeneracy of the level of the hydrogen atom that has the energy* $\left(-\frac{R_H}{9}\right)$?

Solution: $E_n = -\frac{R_H}{n^2} = -\frac{R_H}{9}$

$\therefore$ $n = 3$

Thus, $l = 0$ and $m = 0$ (one 3*s*-orbital)

$l = 1$ and $m = -1, 0, +1$ (three 3*p*-orbitals)

$l = 2$ and $m = -2, -1, 0, +1, +2$ (five 3*d*-orbitals)

Thus, degeneracy is nine $(1 + 3 + 5 = 9$ states$)$.

Example 35. *Calculate the angular frequency of an electron occupying the second Bohr orbit of He⁺ ion.*

Solution: Velocity of electron $(v) = \frac{2\pi Ze^2}{nh}$ ...(i)

Radius of He^+ ion in an orbit $(r_n) = \frac{n^2h^2}{4\pi^2 mZe^2}$ ...(ii)

Angular frequency or angular velocity (ω)

$$= \frac{v}{r_n} = \frac{2\pi Ze^2}{nh} \times \frac{4\pi^2 mZe^2}{n^2h^2} = \frac{8\pi^3 mZ^2e^4}{n^3h^3}$$

Given, $n = 2, m = 9.1 \times 10^{-28}$ g, $Z = 2, e = 4.8 \times 10^{-10}$ esu

$h = 6.626 \times 10^{-27}$ erg-sec

$$\therefore \quad \omega = \frac{8 \times \left(\frac{22}{7}\right)^3 \times 2^2 \times 9.1 \times 10^{-28} \times (4.8 \times 10^{-10})^4}{(2)^3 \times (6.626 \times 10^{-27})^3}$$

$$= 2.067 \times 10^{16}\ \text{sec}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

6. If the speed of electron in first Bohr orbit of hydrogen be 'x', then speed of the electron in second orbit of He^+ is:
(a) $x/2$ (b) $2x$ (c) x (d) $4x$
[Ans. (c)]
[Hint: $v_n = \frac{v_1 \times Z}{n} = \frac{x \times 2}{2} = x$]

7. If first ionisation energy of hydrogen is E, then the ionisation energy of He^+ would be:
(a) E (b) $2E$ (c) $0.5E$ (d) $4E$
[Ans. (d)]
[Hint: $I_2(He^+) = Z^2 I_1(H)$
$= 2^2 \times E = 4E$]

8. The number of spectral lines that are possible when electrons in 7th shell in different hydrogen atoms return to the 2nd shell is:
(a) 12 (b) 15 (c) 14 (d) 10
[Ans. (b)]
[Hint: Number of spectral lines $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$
$= \frac{(7-2)(7-2+1)}{2} = 15$]

9. The ratio of radii of first orbits of H, He^+ and Li^{2+} is:
(a) 1 : 2 : 3 (b) 6 : 3 : 2 (c) 1 : 4 : 9 (d) 9 : 4 : 1
[Ans. (b)]
[Hint: $r = \frac{n^2}{Z} \times 0.529\,\text{Å}$
$r_H : r_{He^+} : r_{Li^{2+}}$
$1 : \frac{1}{2} : \frac{1}{3}$
$6 : 3 : 2$]

10. The energy of second orbit of hydrogen is equal to the energy of:
(a) fourth orbit of He^+ (b) fourth orbit of Li^{2+}
(c) second orbit of He^+ (d) second orbit of Li^{2+}
[Ans. (a)]
[Hint: $E = -\frac{Z^2}{n^2} \times 13.6$ eV
$E_2 = -\frac{13.6}{4}$ for 'H'
$E = -\frac{Z^2}{n^2} \times 13.6$ eV
$-\frac{13.6}{4} = -\frac{Z^2}{n^2} \times 13.6$
$\frac{Z^2}{n^2} = \frac{1}{4}$ $(Z = 1, n = 2)$]

11. What is the energy in eV required to excite the electron from $n = 1$ to $n = 2$ state in hydrogen atom? (n = principal quantum number) **[CET (J&K) 2006]**
(a) 13.6 (b) 3.4 (c) 17 (d) 10.2
[Ans. (d)]
[Hint: $\Delta E = E_2 - E_1$
$= \left(-\frac{13.6}{2^2}\right) - \left(-\frac{13.6}{1^2}\right)$
$= 13.6\left(1 - \frac{1}{4}\right) = \frac{3}{4} \times 13.6 = 10.2$ eV]

12. An electron in an atom undergoes transition in such a way that its kinetic energy changes from x to $\frac{x}{4}$, the change in potential energy will be :
(a) $+\frac{3}{2}x$ (b) $-\frac{3}{8}x$ (c) $+\frac{3}{4}x$ (d) $-\frac{3}{4}x$
[Ans. (a)]

[**Hint** : PE = − 2KE

$\therefore$ PE will change from $-2x$ to $-\frac{2x}{4}$

Change in potential energy $= \left(-\frac{2x}{4}\right) - (-2x)$

$= -\frac{x}{2} + 2x = \frac{3x}{2}$]

2.13 PARTICLE AND WAVE NATURE OF ELECTRON

In 1924, **de Broglie** proposed that an **electron,** like light, behaves both as a material particle and as a wave. This proposal gave birth to a new theory known as **wave mechanical theory of matter.** According to this theory, the electrons, protons and even atoms, when in motion, possess wave properties.

de Broglie derived an expression for calculating the wavelength of the wave associated with the electron.

According to Planck's equation,

$$E = h\nu = h \cdot \frac{c}{\lambda} \quad \ldots (i)$$

The energy of a photon on the basis of Einstein's mass- energy relationship is

$$E = mc^2 \quad \ldots (ii)$$

where, c is the velocity of the electron.

Equating both the equations, we get

$$h\frac{c}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

Momentum of the moving electron is inversely proportional to its wavelength.

Let kinetic energy of the particle of mass 'm' is E.

$$E = \frac{1}{2}mv^2$$

$$2Em = m^2v^2$$

$$\sqrt{2Em} = mv = p(\text{momentum})$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}}$$

Davisson and **Germer** made the following modification in de Broglie equation:

Let a charged particle, say an electron be accelerated with a potential of V; then the kinetic energy may be given as:

$$\frac{1}{2}mv^2 = eV$$

$$m^2v^2 = 2eVm$$

$$mv = \sqrt{2eVm} = p$$

$$\lambda = \frac{h}{\sqrt{2eVm}}$$

$$\lambda = \frac{h}{\sqrt{2qVm}} \text{ for charged particles of charge } q$$

de Broglie waves are not radiated into space, *i.e.*, they are always associated with electron. The wavelength decreases if the value of mass (m) increases, *i.e.*, in the case of heavier particles, the wavelength is too small to be measured. de Broglie equation is applicable in the case of smaller particles like electron and has no significance for larger particles.

(A) de Broglie wavelength associated with charged particles

(i) For electron:

$$\lambda = \frac{12.27}{\sqrt{V}} \text{Å}$$

(ii) For proton:

$$\lambda = \frac{0.286}{\sqrt{V}} \text{Å}$$

(iii) For α-particles:

$$\lambda = \frac{0.101}{\sqrt{V}} \text{Å}$$

where, V = accelerating potential of these particles.

(B) de Broglie wavelength associated with uncharged particles

(i) For neutrons:

$$\lambda = \frac{h}{\sqrt{2Em}} = \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times E}}$$

$$= \frac{0.286}{\sqrt{E\,(\text{eV})}} \text{Å}$$

(ii) For gas molecules:

$$\lambda = \frac{h}{m \times v_{\text{rms}}}$$

$$= \frac{h}{\sqrt{3mkT}}$$

where, k = Boltzmann constant

Bohr theory versus de Broglie equation: One of the postulates of Bohr theory is that angular momentum of an electron is an integral multiple of $\frac{h}{2\pi}$. This postulate can be derived with the help of de Broglie concept of wave nature of electron.

Consider an electron moving in a circular orbit around nucleus. The wave train would be associated with the circular orbit as shown in Fig. 2.15. If the two ends of an electron wave meet to give a regular series of crests and troughs, the electron wave is said to be in phase, *i.e.*, the circumference of Bohr orbit is equal to whole number multiple of the wavelength of the electron wave.

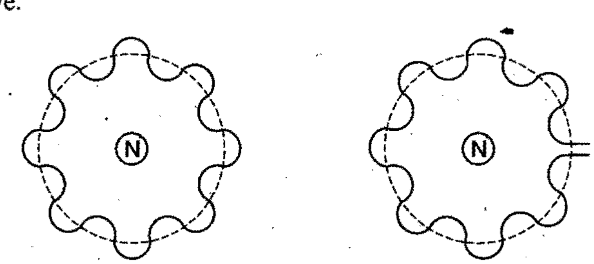


Fig. 2.15

So, $2\pi r = n\lambda$

or $$\lambda = \frac{2\pi r}{n} \quad \ldots \text{(i)}$$

From de Broglie equation,

$$\lambda = \frac{h}{mv} \quad \ldots \text{(ii)}$$

Thus, $$\frac{h}{mv} = \frac{2\pi r}{n}$$

or $$mvr = n \cdot \frac{h}{2\pi}$$ (v = velocity of electron and r = radii of the orbit)

i.e., $$\text{Angular momentum} = n \cdot \frac{h}{2\pi} \quad \ldots \text{(iii)}$$

This proves that the de Broglie and Bohr concepts are in perfect agreement with each other.

2.14 HEISENBERG UNCERTAINTY PRINCIPLE

Bohr theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave is extending throughout a region of space. To locate the electron, radiation with extremely short wavelength is required. Radiation that has short wavelength is very energetic in nature. When it strikes the electron, the impact causes a change in the velocity of the electron. Thus, the attempt to locate the electron changes ultimately the momentum of the electron. Photons with longer wavelengths are less energetic and cause less effect on the momentum of the electron. Because of larger wavelength, such photons are not able to locate the position of an electron precisely.

In 1927, **Werner Heisenberg** presented a principle known as **Heisenberg uncertainty principle** which states: **"It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron."**

The uncertainty of measurement of position, Δx and the uncertainty of momentum, Δp or Δmv are related by Heisenberg's relationship as:

$$\Delta x \cdot \Delta p \geq h/4\pi$$

or $$\Delta x \cdot \Delta mv \geq h/4\pi$$

where, h is Planck's constant.

For an electron of mass $m\,(9.10 \times 10^{-28}$ g), the product of uncertainty is quite large.

$$\Delta x \cdot \Delta v \geq \frac{6.626 \times 10^{-27}}{4\pi m}$$

$$\geq \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}}$$

$$\approx 0.57 \text{ erg-sec per gram approximately}$$

$\Delta x \cdot \Delta v$ = uncertainty product

When $\Delta x = 0, \Delta v = \infty$ and *vice-versa*.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, *i.e.*, Δx is very small, Δv becomes large and *vice-versa*. Thus, uncertainty principle is important only in the case of smaller moving particles like electrons.

For other canonical conjugates of motion, the equation for Heisenberg uncertainty principle may be given as:

$$\text{momentum} = \text{mass} \times \text{velocity}$$

$$= \text{mass} \times \frac{\text{velocity}}{\text{time}} \times \text{time}$$

$$= \text{force} \times \text{time}$$

$$\text{momentum} \times \text{distance} = \text{force} \times \text{distance} \times \text{time}$$

$$= \text{energy} \times \text{time}$$

$$\Delta p\, \Delta x = \Delta E\, \Delta t$$

$$\Delta E\, \Delta t \geq \frac{h}{4\pi} \quad \text{(for energy and time)}$$

Similarly, $$\Delta \phi\, \Delta \theta \geq \frac{h}{4\pi} \quad \text{(for angular motion)}$$

On the basis of this principle, therefore, Bohr picture of an electron in an atom, which gives a fixed position in a fixed orbit and definite velocity to an electron, is no longer tenable. The best we can think of in terms of probability of locating an electron with a probable velocity in a given region of space at a given time. The space or a three dimensional region round the nucleus where there is maximum probability of finding an electron of a specific energy is called an **atomic orbital**.

SOME SOLVED EXAMPLES

Example 36. *Calculate the wavelength associated with an electron moving with a velocity of 10^{10} cm per sec.*

Solution: Mass of the electron $= 9.10 \times 10^{-28}$ g

Velocity of electron $= 10^{10}$ cm per sec

$h = 6.62 \times 10^{-27}$ erg-sec

According to de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-27}}{9.10 \times 10^{-28} \times 10^{10}}$$

$$= 7.72 \times 10^{-10} \text{ cm}$$

$$= 0.0772 \text{ Å}$$

Example 37. *Calculate the uncertainty in the position of a particle when the uncertainty in momentum is:*
(a) 1×10^{-3} *g cm sec^{-1} (b) zero.*

Solution: (a) Given,

$\Delta P = 1 \times 10^{-3}$ g cm sec^{-1}

$h = 6.62 \times 10^{-27}$ erg-sec

$\pi = 3.142$

According to uncertainty principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

So, $$\Delta x \geq \frac{h}{4\pi} \cdot \frac{1}{\Delta p} \geq \frac{6.62 \times 10^{-27}}{4 \times 3.142} \times \frac{1}{10^{-3}}$$

$$= 0.527 \times 10^{-24} \text{ cm}$$

(b) When the value of $\Delta p = 0$, the value of Δx will be infinity.

Example 38. *Calculate the momentum of a particle which has a de Broglie wavelength of* 2.5×10^{-10} *m.* ($h = 6.6 \times 10^{-34}$ $kg\ m^2\ s^{-1}$)

Solution: Momentum $= \frac{h}{\lambda}$ (using de Broglie equation)

$$= \frac{6.6 \times 10^{-34}}{2.5 \times 10^{-10}}$$

$$= 2.64 \times 10^{-24} \text{ kg m sec}^{-1}$$

Example 39. *What is the mass of a photon of sodium light with a wavelength of* $5890\ \mathring{A}$*?* ($h = 6.63 \times 10^{-27}$ *erg - sec*, $c = 3 \times 10^{10}$ *cm / sec*)

Solution: $\lambda = \frac{h}{mc}$

or $m = \frac{h}{\lambda c}$

So, $m = \frac{6.63 \times 10^{-27}}{5890 \times 10^{-8} \times 3 \times 10^{10}}$

$$= 3.752 \times 10^{-33} \text{ g}$$

Example 40. *The uncertainty in position and velocity of a particle are* 10^{-10} *m and* 5.27×10^{-24} $m s^{-1}$ *respectively. Calculate the mass of the particle.* ($h = 6.625 \times 10^{-34}$ $J - s$)

Solution: According to Heisenberg's uncertainty principle,

$$\Delta x \cdot m\,\Delta v = \frac{h}{4\pi}$$

or $m = \frac{h}{4\pi\ \Delta x \cdot \Delta v}$

$$= \frac{6.625 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 5.27 \times 10^{-24}}$$

$$= 0.099 \text{ kg}$$

Example 41. *Calculate the uncertainty in velocity of a cricket ball of mass* 150 g *if the uncertainty in its position is of the order of* $1\ \mathring{A}$ ($h = 6.6 \times 10^{-34}$ $kg\ m^2\ s^{-1}$).

Solution: $\Delta x \cdot m\,\Delta v = \frac{h}{4\pi}$

$$\Delta v = \frac{h}{4\pi\ \Delta x \cdot m}$$

$$= \frac{6.6 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 0.150}$$

$$= 3.499 \times 10^{-24} \text{ ms}^{-1}$$

Example 42. *Find the number of waves made by a Bohr electron in one complete revolution in the 3rd orbit.* **(IIT 1994)**

Solution: Velocity of the electron in 3rd orbit $= \frac{3h}{2\pi mr}$

where, m = mass of electron and r = radius of 3rd orbit.

Applying de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{h}{m} \times \frac{2\pi mr}{3h} = \frac{2\pi r}{3}$$

$$\text{No. of waves} = \frac{2\pi r}{\lambda} = \frac{2\pi r}{2\pi r} \times 3 = 3$$

Example 43. *The kinetic energy of an electron is* 4.55×10^{-25} *J. Calculate the wavelength,* ($h = 6.6 \times 10^{-34}$ *J-sec, mass of electron* $= 9.1 \times 10^{-31}$ *kg*).

Solution: $KE = \frac{1}{2} mv^2 = 4.55 \times 10^{-25}$

or $\frac{1}{2} \times 9.1 \times 10^{-31} \times v^2 = 4.55 \times 10^{-25}$

or $v^2 = \frac{2 \times 4.55 \times 10^{-25}}{9.1 \times 10^{-31}}$

$$v = 10^3 \text{ ms}^{-1}$$

Applying de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3} = 0.72 \times 10^{-6} \text{ m}$$

Example 44. *The speeds of the Fiat and Ferrari racing cars are recorded to* $\pm 4.5 \times 10^{-4}$ $m\,sec^{-1}$. *Assuming the track distance to be known within* $\pm 16\,m$, *is the uncertainty principle violated for a* 3500 *kg car?*

Solution: $\Delta x\,\Delta v = 4.5 \times 10^{-4} \times 16$

$$= 7.2 \times 10^{-3} \text{ m}^2 \text{ sec}^{-1} \quad \ldots\text{(i)}$$

$$\frac{h}{4\pi m} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 3500} \quad \ldots\text{(ii)}$$

$$= 1.507 \times 10^{-38}$$

Since, $\Delta x\,\Delta v \geq h / 4\pi m$

Hence, Heisenberg uncertainty principle is not violated.

Example 45. *Alveoli are tiny sacs in the lungs whose average diameter is* 5×10^{-5} *m. Consider an oxygen molecule* (5.3×10^{-26} *kg*) *trapped within a sac. Calculate uncertainty in the velocity of oxygen molecule.*

Solution: Uncertainty in position Δx = Diameter of Alveoli

$$= 5 \times 10^{-10} \text{ m}$$

$$\Delta x\,\Delta v \geq \frac{h}{4\pi m}$$

$$\Delta v \geq \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 5.3 \times 10^{-26} \times 5 \times 10^{-10}}$$

$$\Delta v \approx 1.99 \text{ m / sec}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

13. If the kinetic energy of an electron is increased 4 times, the wavelength of the de Broglie wave associated with it would become:

(a) 4 times (b) 2 times

(c) $\frac{1}{2}$ times (d) $\frac{1}{4}$ times

[Ans. (c)]

[Hint: $\lambda = \frac{h}{\sqrt{2Em}}$, where, E = kinetic energy

When, the kinetic energy of electron becomes 4 times, the de Broglie wavelength will become half.]

14. The mass of photon having wavelength 1 nm is:

(a) 2.21×10^{-35} kg (b) 2.21×10^{-33} g

(c) 2.21×10^{-33} kg (d) 2.21×10^{-26} kg

[Ans. (c)]

[Hint: $\lambda=\dfrac{h}{mc}$

$$m=\frac{h}{\lambda c}=\frac{6.626\times10^{-34}}{1\times10^{-9}\times3\times10^{8}}$$

$$=2.21\times10^{-33}\text{ kg}]$$

15. The de Broglie wavelength of 1 mg grain of sand blown by a 20 ms^{-1} wind is:

(a) 3.3×10^{-29} m (b) 3.3×10^{-21} m

(c) 3.3×10^{-49} m (d) 3.3×10^{-42} m

[Ans. (a)]

[Hint: $\lambda=\dfrac{h}{mv}=\dfrac{6.626\times10^{-34}}{1\times10^{-6}\times20}=3.313\times10^{-29}$ m]

16. In an atom, an electron is moving with a speed of 600 m sec^{-1} with an accuracy of 0.005%. Certainty with which the position of the electron can be located is:

($h=6.6\times10^{-34}$ kg m^2 s^{-1}, mass of electron $=9.1\times10^{-31}$ kg)

(AIEEE 2009)

(a) 1.52×10^{-4} m (b) 5.1×10^{-3} m

(c) 1.92×10^{-3} m (d) 3.84×10^{-3} m

[Ans. (c)]

[Hint: Accuracy in velocity = 0.005%

$$\Delta v=\frac{600\times0.005}{100}=0.03$$

According to Heisenberg's uncertainty principle,

$$\Delta x\, m\Delta v\ge\frac{h}{4\pi}$$

$$\Delta x=\frac{6.6\times10^{-34}}{4\times3.14\times9.1\times10^{-31}\times0.03}$$

$$=1.92\times10^{-3}\text{ m}]$$

17. Velocity of de Broglie wave is given by:

(a) $\dfrac{c^2}{\nu}$ (b) $\dfrac{h\nu}{mc}$ (c) $\dfrac{mc^2}{h}$ (d) $\nu\lambda$

[Ans. (b)]

[Hint: $\lambda=\dfrac{h}{mv}=\dfrac{h}{p}$

$$p=\frac{h}{\lambda}$$

$$mv=\frac{h\nu}{c}$$

$$v=\frac{h\nu}{mc}]$$

2.15 WAVE MECHANICAL MODEL OF ATOM

The atomic model which is based on the particle and wave nature of the electron is known as **wave mechanical model of the atom.** This was developed by **Erwin Schrödinger** in 1926. This model describes the electron as a three-dimensional wave in the electronic field of positively charged nucleus. Schrödinger derived an equation which describes wave motion of an electron. The differential equation is:

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}+\frac{8\pi^2m}{h^2}(E-V)\psi=0$$

where, x, y and z are cartesian coordinates of the electron; m = mass of the electron; E = total energy of the electron; V = potential energy of the electron; h = Planck's constant and ψ(psi) = wave function of the electron.

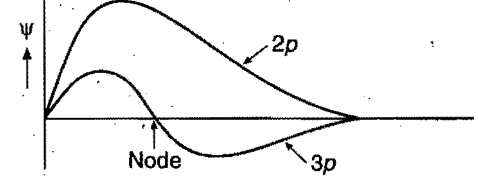
Significance of ψ: The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y and z. The wave function may have positive or negative values depending upon the values of coordinates.

The main aim of Schrödinger equation is to give a solution for the probability approach. When the equation is solved, it is observed that for some regions of space the value of ψ is positive and for other regions the value of ψ is negative. But the probability must be always positive and cannot be negative. It is, thus, proper to use ψ^2 in favour of ψ.

Significance of ψ^2: ψ^2 is a probability factor. It describes the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is termed as orbital.

The solution of the wave equation is beyond the scope of this book. The important point of the solution of this equation is that it provides a set of numbers, called **quantum numbers,** which describe energies of the electrons in atoms, information about the shapes and orientations of the most probable distribution of electrons around the nucleus.

Wave function ψ can be plotted against distance 'r' from nucleus as,



For hydrogen wave function, number of nodes can be calculated as,

(i) Number of radial nodes = $(n - l - 1)$
(ii) Number of angular nodes = l
(iii) Total number of nodes = $(n - 1)$
(iv) Number of nodal planes = l

Note: If the node at $r = \infty$ is also considered then no. of nodes will be 'n' (not $n - 1$).

Examples: (*i*) *For 1s-orbital* $n = 1,\ l = 0$, *it will have no radial or angular node.*

(*ii*) *For 2s-orbital,* $n = 2,\ l = 0$, *it will have only one radial node.*

(*iii*) *For 3s-orbital,* $n = 3,\ l = 0$, *it will have two radial nodes.*

(*iv*) *For 2p-orbital,* $n = 2,\ l = 1$, *it will have no radial node but it has only one angular node.*

(*v*) *For 3p-orbital,* $n = 3,\ l = 1$, *it will have one radial and one angular node.*

For *s*-orbitals:
$(n - 1)$ radial nodes + 0 angular node = $(n - 1)$ total nodes.

For *p*-orbitals:
$(n - 2)$ radial nodes + 1 angular node = $(n - 1)$ total nodes.

For *d*-orbitals:
$(n - 3)$ radial nodes + 2 angular nodes = $(n - 1)$ total nodes.

d_{z^2} like all d-orbitals has two angular nodes. The difference is that the angular nodes are cones in a d_{z^2} orbital, not planes.

Operator form Schrödinger Wave Equation

$$\hat{H}\Psi = E\Psi \qquad \text{(Operator form)}$$

$$\text{where } \hat{H} = \left[-\frac{h^2}{8\pi^2 m}\nabla^2 + \hat{V}\right] = \text{Hamiltonian operator}$$

$$= \hat{T} + \hat{V}$$

Here, $\hat{T}$ = Kinetic energy operator
$\hat{V}$ = Potential energy operator

Complete wave function can be given as

$$\Psi(r, \theta, \phi) = \underbrace{R(r)}_{\text{Radial part}} \quad \underbrace{\Theta(\theta)\Phi(\phi)}_{\text{Angular part}}$$

Dependence of the wave function on quantum number can be given as,

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\ \Theta_{lm}(\theta)\Phi_m(\phi)$$

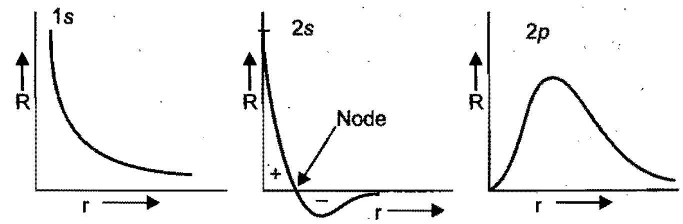
The function R depend only on r, therefore they describe the distribution of the electron as a function of r from the nucleus. These functions depend upon two quantum numbers, n and l. The two functions Θ and Φ taken together give the angular distribution of the electron.

The radial part of the wave function for some orbitals may be given as,

	n	l	R_{nl}
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2s	2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2p	2	1	$\frac{1}{\sqrt{3}}\left(\frac{Zr}{2a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$

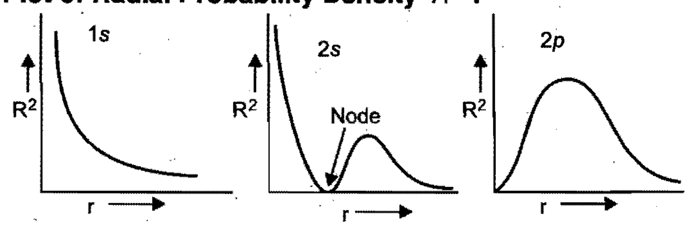
where, Z = atomic number, a_0 = radius of first Bohr orbit of hydrogen.

Plot of Radial Wave Function '*R*' :



Number of radial nodes = $(n - l - 1)$.
At node, the value of 'R' changes from positive to negative.

Plot of Radial Probability Density 'R^2':

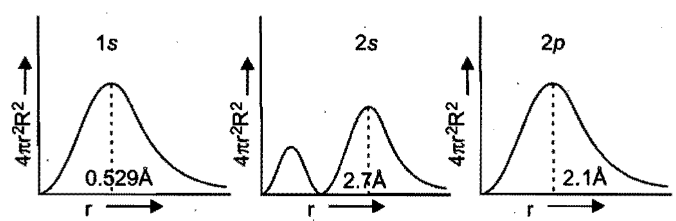


The plots of probability, *i.e.*, R^2 or Ψ^2 are more meaningful than the plots of functions themselves. It can be seen that for both 1*s* and 2*s* orbitals, the probability has a maximum value at $r = 0$, *i.e.*, in the nucleus. In case of 2*s* orbital, one more maximum in the probability plot is observed.

Plot of Radial Probability Function $(4\pi r^2 R^2)$:

In order to visualize the electron cloud within a spherical shell is placed at radii 'r' and '$r + dr$' from the nucleus. Thus radial probability function describes the total probability of finding the electron in a spherical shell of thickness 'dr' located at the distance r from the nucleus.

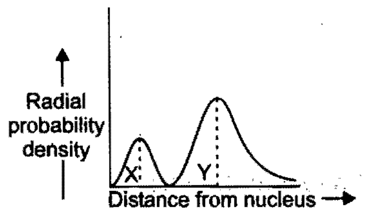
R.P.F. = (Volume of spherical shell) × Probability density
$= (4\pi r^2 dr) \times R^2$



In the plot of radial probability against 'r', number peaks, *i.e.*, region of maximum probability = $n - l$.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

18.



If the above radial probability curve indicates '2s' orbital, the distance between the peak points X, Y is :

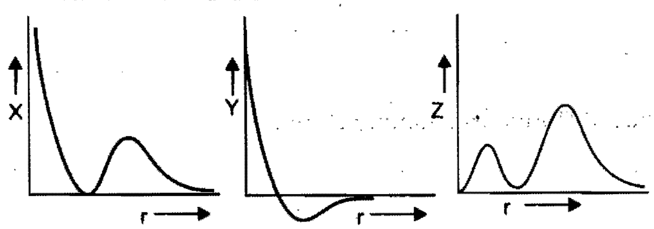
(a) 2.07Å (b) 1.59Å (c) 0.53Å (d) 2.12Å

[Ans. (a)]

[**Hint :** $X = 0.53Å,\ Y = 2.6Å$

$Y - X = 2.6 - 0.53 = 2.07Å$]

19. Plots for 2s orbital are :



X, Y and Z are respectively

(a) R, R^2 and $4\pi r^2 R^2$ (b) R^2, R and $4\pi r^2 R^2$

(c) $4\pi r^2 R^2, R^2$ and R (d) $R^2, 4\pi r^2 R^2$ and R

[Ans. (b)]

[**Hint :** Y will be definitely 'R' because value of R cannot be negative, thus X will be R^2 and Z will be $4\pi r^2 R$. Z represents radial probability function; its value will be zero at origin]

20. The wave function (Ψ) of 2s is given by :

$$\Psi_{2s} = \frac{1}{2\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{1/2}\left\{2 - \frac{r}{a_0}\right\} e^{-r/2a_0}$$

At $r = r_0$, radial node is formed. Thus for 2s, r_0 in terms of a_0 is :

(a) $r_0 = a_0$ (b) $r_0 = 2a_0$ (c) $r_0 = a_0/2$ (d) $r_0 = 4a_0$

[Ans. (b)]

[**Hint :** When $r = r_0$, $\psi_{2s} = 0$, then from the given equation:

$$2 - \frac{r}{a_0} = 0$$

$$r = 2a_0]$$

21. The wave function for 1s orbital of hydrogen atom is given by :

$$\Psi_{1s} = \frac{\pi}{\sqrt{2}} e^{-r/a_0}$$

where, a_0 = Radius of first Bohr orbit

r = Distance from the nucleus (Probability of finding the electron varies with respect to it)

What will be the ratio of probabilities of finding the electrons at the nucleus to first Bohr's orbit a_0?

(a) e (b) e^2 (c) $1/e^2$ (d) zero

[Ans. (d)]

[**Hint :** For 1s orbital, probability of finding the electron at the nucleus is zero.]

22. The radial wave equation for hydrogen atom is :

$$\Psi = \frac{1}{16\sqrt{4}}\left(\frac{1}{a_0}\right)^{3/2}[(x-1)(x^2 - 8x + 12)]e^{-x/2}$$

where, $x = 2r/a_0$; a_0 = radius of first Bohr orbit.

The minimum and maximum position of radial nodes from nucleus are :

(a) $a_0, 3a_0$ (b) $\frac{a_0}{2}, 3a_0$ (c) $\frac{a_0}{2}, a_0$ (d) $\frac{a_0}{2}, 4a_0$

[Ans. (b)]

[**Hint :** At radial node, $\Psi = 0$

∴ From given equation,

$$x - 1 = 0 \text{ and } x^2 - 8x + 12 = 0$$

$$x - 1 = 0 \Rightarrow x = 1$$

i.e., $\frac{2r}{a_0} = 1;\ r = \frac{a_0}{2}$ (Minimum)

$$x^2 - 8x + 12 = 0$$

$$(x-6)(x-2) = 0$$

when $x - 2 = 0$

$$x = 2$$

$\frac{2r}{a_0} = 2$, *i.e.,* $r = a_0$ (Middle value)

when $x - 6 = 0$

$$x = 6$$

$$\frac{2r}{a_0} = 6$$

$r = 3a_0$ (Maximum)]

2.16 QUANTUM NUMBERS

As we know, to search a particular person in this world, four things are needed:

(i) The country to which the person belongs

(ii) The city in that country to which the person belongs

(iii) The street in that city where the person is residing

(iv) The house number

Similarly, four identification numbers are required to locate a particular electron in an atom. These identification numbers are called **quantum numbers.** The four quantum numbers are discussed below.

Principal Quantum Number

It was given by **Bohr;** it is denoted by 'n'. It represents the name, size and energy of the shell to which the electron belongs.

The value of 'n' lies between 1 to ∞.

$$n = 1, 2, 3, 4, \ldots \infty$$

Value of n	=	1	2	3	4	5	6	7
Designation of shell	=	K	L	M	N	O	P	Q

(i) Higher is the value of 'n', greater is the distance of the shell from the nucleus.

$$r_1 < r_2 < r_3 < r_4 < r_5 < \ldots$$

$$r = \frac{n^2}{Z} \times 0.529 \text{ Å}$$

(ii) Higher is the value of 'n', greater is the magnitude of energy.

$$E_1 < E_2 < E_3 < E_4 < E_5 \ldots$$

$$E = -\frac{Z^2}{n^2} \times 21.69 \times 10^{-19} \text{ J/atom}$$

$$= -\frac{Z^2}{n^2} \times 313.3 \text{ kcal per mol}$$

Energy separation between two shells decreases on moving away from nucleus.

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > (E_5 - E_4)$$

(iii) Maximum number of electrons in a shell* $= 2n^2$

(iv) Angular momentum can also be calculated using principal quantum number

$$mvr = \frac{nh}{2\pi}$$

Azimuthal Quantum Number

It was given by **Sommerfeld;** it is also called **angular quantum number, subsidiary quantum number** or **secondary quantum number.** It is denoted by 'l'; its value lies between 0, 1, 2, . . . $(n-1)$.

It describes the spatial distribution of electron cloud and angular momentum. It gives the name of the subshell associated with the main shell

$l = 0$ s-subshell; $l = 1$ p-subshell;
$l = 2$ d-subshell; $l = 3$ f-subshell;
$l = 4$ g-subshell.

s, p, d, f and g are spectral terms and signify *sharp, principal, diffused, fundamental* and *generalised* respectively.

The energies of the various subshells in the same shell are in the order of $s < p < d < f < g$ (increasing order). Subshells having equal l values but with different n values have similar shapes but their sizes increase as the value of 'n' increases. 2s-subshell is greater in size than 1s-subshell. Similarly $2p, 3p, 4p$-subshells have similar shapes but their sizes increase in the order $2p < 3p < 4p$.

Orbital angular momentum of an electron is calculated using the expression

$$\mu_l = \sqrt{l(l+1)}\frac{h}{2\pi} = \sqrt{l(l+1)}\,\hbar$$

here, $\hbar = \dfrac{h}{2\pi}$

The magnitude of magnetic moment μ_L may be given as:

$$\mu_L = \sqrt{l(l+1)} \text{ BM}$$

where, BM = Bohr Magneton

$$1 \text{ BM} = \frac{eh}{4\pi mc} = 9.2732 \times 10^{-14} \text{ J}$$

Maximum electrons present in a subshell $= 2(2l+1)$

s-subshell $\rightarrow$ 2 electrons d-subshell $\rightarrow$ 10 electrons
p-subshell $\rightarrow$ 6 electrons f-subshell $\rightarrow$ 14 electrons
g-subshell $\rightarrow$ 18 electrons

Magnetic Quantum Number

This quantum number is designated by the symbol 'm'. To explain splitting of a single spectral line into a number of closely spaced lines in the presence of magnetic field **(Zeeman effect),** Linde proposed that electron producing a single line has several possible space orientations for the same angular momentum vector in a magnetic field, *i.e.*, under the influence of magnetic field each subshell is further sub-divided into orbitals. Magnetic quantum number describes the orientation or distribution of electron cloud. For each value of 'l', the magnetic quantum number 'm' may assume all integral values from $-l$ to $+l$ including zero, *i.e.*, total $(2l+1)$ values.

Thus, when $l = 0, m = 0$ (only one value)
when $l = 1, m = -1, 0, +1$ (three values)
i.e., three orientations.

One orientation corresponds to one orbital. Three orientations (orbitals) are designated as p_x, p_y and p_z.

When $l = 2, m = -2, -1, 0, +1, +2$ (five values), *i.e.*, five orientations.

The five orbitals are designated as:

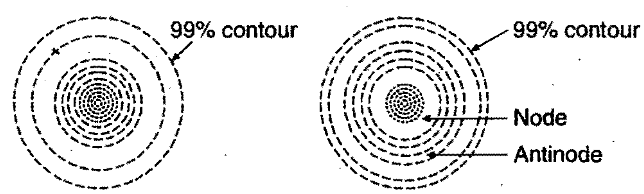
$$d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2} \text{ and } d_{z^2}.$$

When $l = 3, m = -3, -2, -1, 0, +1, +2, +3$ (seven values), *i.e.*, seven orientations.

Different values of 'm' for a given value of 'l' provide the total number of ways in which a given s, p, d and f subshells in presence of magnetic field can be arranged in space along x, y and z axes or total number of orbitals into which a given subshell can be divided.

When $l = 0, m = 0$, *i.e.*, one value implies that 's' subshell has only one space orientation and hence, it can be arranged in space only in one way along x, y or z axes. Thus, 's' orbital has a symmetrical spherical shape and is usually represented as in Fig. 2.16.

In case of 1s-orbital, the electron cloud is maximum at the nucleus and decreases with the distance. The electron density at a particular distance is uniform in all directions. The region of maximum electron density is called **antinode.** In case of '2s'-orbital, the electron density is again maximum at the nucleus and decreases with increase in distance. The '2s'-orbital differs in detail from a 1s-orbital. The electron in a '2s'-orbital is likely to be found in two regions, one near the nucleus and other in a spherical shell about the nucleus. Electron density is zero in nodal region.



1s 2s-orbital

*No energy shell in atoms of known elements possesses more than 32 electrons.

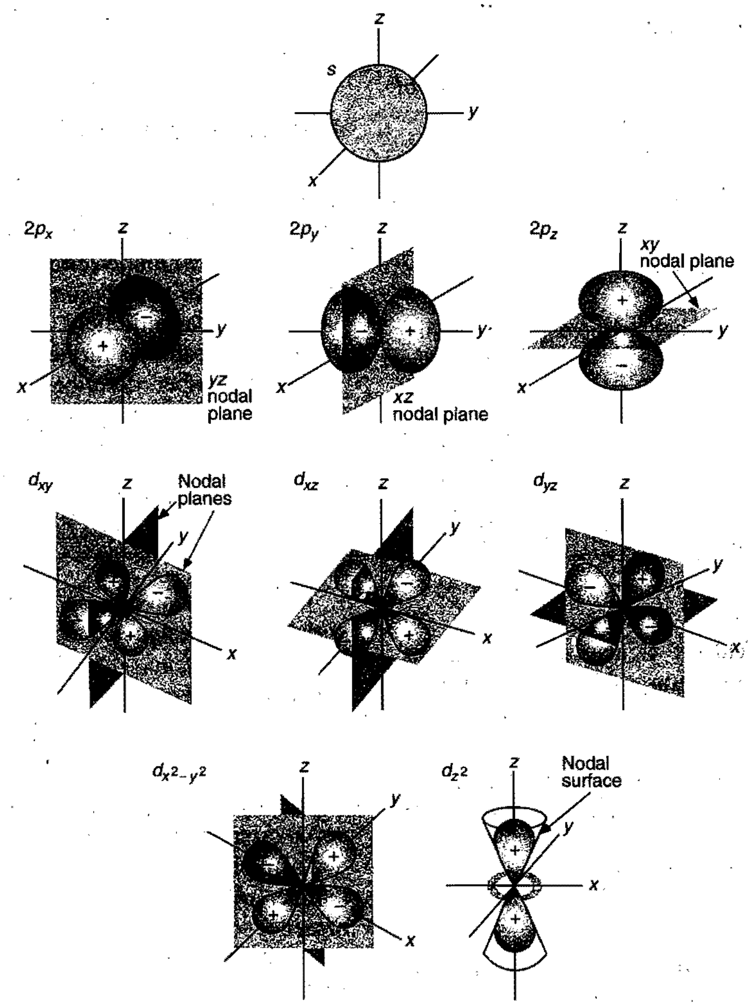


Fig. 2.16

When $l = 1$, 'm' has three values $-1, 0, +1$. It implies that 'p' subshell of any energy shell has three space orientations, *i.e.*, three orbitals. Each p-orbital has **dumb-bell** shape. Each one is disposed symmetrically along one of the three axes as shown in Fig. 2.16. p-orbitals have directional character.

Orbital	p_z	p_x	p_y
m	0	± 1	± 1
Nodal plane	xy	yz	zx

When $l = 2$, 'm' has five values $-2, -1, 0, +1, +2$. It implies that d-subshell of any energy shell has five orientations, *i.e.*, five orbitals. All the five orbitals are not identical in shape. Four of the d-orbitals $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ contain four lobes while fifth orbital d_{z^2} consists of only two lobes. The lobes of d_{xy} orbital lie between x and y-axes. Similar is the case for d_{yz} and d_{zx}. Four lobes of $d_{x^2-y^2}$ orbital are lying along x and y-axes while the two lobes of d_{z^2} orbital are lying along z-axis and contain a ring of negative charge surrounding the nucleus in xy-plane (Fig. 2.16).

Orbital	d_{xy}	d_{yz}	d_{zx}	$d_{x^2-y^2}$	d_{z^2}
m	± 2	± 1	± 1	± 2	0

Nodal planes :

Orbital	Nodal planes
d_{xy}	xz, yz
d_{yz}	xy, zx
d_{zx}	xy, yz
$d_{x^2-y^2}$	$x - y = 0, x + y = 0$
d_{z^2}	No nodal plane, it has a ring around the lobe

There are seven f-orbitals designated as $f_{x(x^2-y^2)}, f_{y(x^2-y^2)}, f_{z(x^2-y^2)}, f_{xyz}, f_{z^3}, f_{yz^2}$ and f_{xz^2}. Their shapes are complicated ones.

Positive values of m_l describes the orbital angular momentum component in the direction of applied magnetic field while the negative values of m_l are for the components in opposite direction to the applied magnetic field.

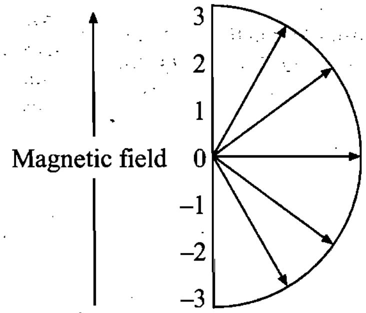


Fig. 21.6 (a) Space quantization in magnetic field

Characteristics of Orbitals

(i) All orbitals of the same shell in the absence of magnetic field possess same energy, *i.e.*, they are **degenerate.**

(ii) All orbitals of the same subshell differ in the direction of their space orientation.

(iii) Total number of orbitals in a main energy shell is equal to n^2 (but not more than 16 in any of the main shells of the known elements).

$n = 1$ No. of orbitals $= (1)^2 = 1\,(1s)$

$n = 2$ No. of orbitals $= (2)^2 = 4\,(2s, 2p_x, 2p_y, 2p_z)$

$n = 3$ No. of orbitals $= (3)^2 = 9\,(3s, 3p_x, 3p_y, 3p_z, 3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x^2-y^2}, 3d_{z^2})$

$n = 4$ No. of orbitals $= (4)^2 = 16$

The division of main shells into subshells and that of subshell into orbitals has been shown below:

Note: Magnetic quantum number also represents quantized value of z-component of angular momentum of the electron in an orbital through the expression

$$Lz = m\left(\frac{h}{2\pi}\right)$$

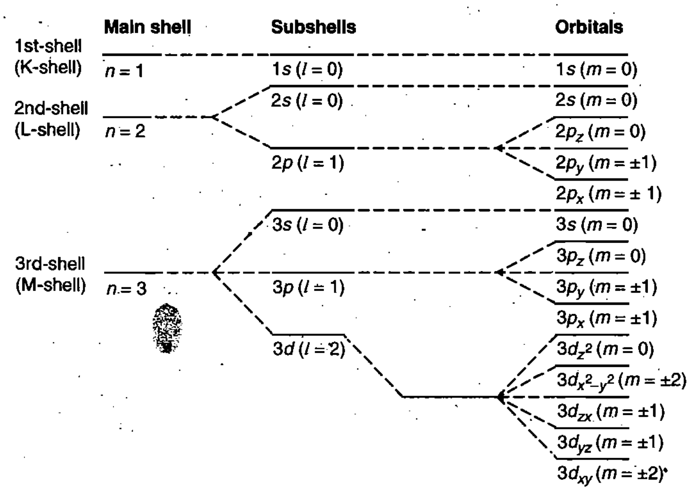
If θ is the angle between z-axis and angular momentum vector,

$$Lz = L\cos\theta$$

$$m\left(\frac{h}{2\pi}\right) = \sqrt{l(l+1)}\,\frac{h}{2\pi}\cos\theta$$

or

$$m = \sqrt{l(l+1)}\cos\theta$$



Degenerate Orbitals

Orbitals which are located at the same energy level on the energy level diagram are called degenerate orbitals. Thus, electrons have equal probability to occupy any of the degenerate orbitals.

p_x, p_y and $p_z \longrightarrow$ 3-fold degenerate

d-orbitals $\longrightarrow$ 5-fold degenerate

f-orbitals $\longrightarrow$ 7-fold degenerate

Degeneracy of p-orbitals remains unaffected in presence of external uniform magnetic field but degeneracy of d and f-orbitals is affected by external magnetic field.

Spin Quantum Number

It is denoted by 's' and it was given by **Goldschmidt.**

Spin quantum number represents the direction of electron spin around its own axis.

(i) For clockwise spin, $s = +\frac{1}{2}$ ($\uparrow$ arrow representation).

(ii) For anticlockwise spin, $s = -\frac{1}{2}$ ($\downarrow$ arrow representation).

Spin electron produces angular momentum equal to μ_s given by

$$\mu_s = \sqrt{s(s+1)}\,\frac{h}{2\pi}, \text{ where, } s = +\tfrac{1}{2}$$

Total spin of an atom $= n \times \frac{1}{2}$ (n = number of unpaired electrons)

Spin magnetic moment (μ_s) is given by

$$\mu_s = \sqrt{s(s+1)}\,\frac{eh}{2\pi mc}$$

Each orbital can accommodate two electrons with opposite spin or spin paired; paired electrons cancel the magnetic moment and develop mutual magnetic attraction as shown in the following Fig. 2.17.

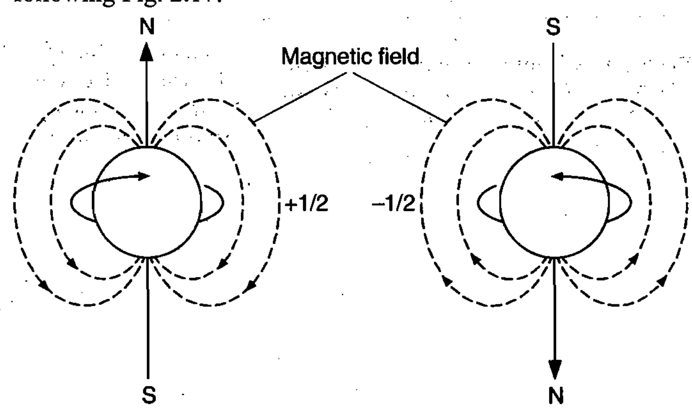


Fig. 2.17

Electrons having same spin are called spin parallel and those having opposite spin are called spin paired.

Spin paired $\longrightarrow$ $\boxed{\uparrow\downarrow}$

Spin parallel $\longrightarrow$ $\boxed{\uparrow\uparrow}$

Spin multiplicity:

Spin multiplicity $= [2\Sigma s + 1]$

where, s = spin quantum number

		$1s^2$	$2s^2$	$2p^2$		
e.g., carbon	=					
Normal state	=	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	
Excited state	=	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$

$$\text{Spin multiplicity} = 2\left[\left(+\frac{1}{2}\right)5+\left(-\frac{1}{2}\right)\right]+1=5$$

2.17 PAULI'S EXCLUSION PRINCIPLE

Each electron in an atom is designated by a set of four quantum numbers. In 1925, Pauli proposed that *no two electrons in an atom can have same values of all the four quantum numbers.*

An orbital accommodates two electrons with opposite spin; these two electrons have same values of principal, azimuthal and magnetic quantum number but the fourth, *i.e.*, spin quantum number will be different.

This principle can be illustrated by taking example of nitrogen.

$$N_7 = 1s^2\ ;\ 2s^2\ ;\ 2p^3$$

$$= 1s^2\ ;\ 2s^2\ ;\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

$$= \boxed{\uparrow\downarrow}\ ;\ \boxed{\uparrow\downarrow}\ ;\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$$

Principal quantum number (n)	1	2	2	2	2
Azimuthal quantum number (l)	0	0	1	1	1
Magnetic quantum number (m)	0	0	+1	−1	0
Spin quantum number (s)	$+\frac{1}{2}-\frac{1}{2}$;	$+\frac{1}{2}-\frac{1}{2}$;	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$

Out of seven electrons no two have same values of all four quantum numbers. With the help of this principle, it is possible to calculate the maximum number of electrons which can be accommodated on main energy shells and subshells.

Principal Q. No. 'n'	Azimuthal Q. No. 'l'	Magnetic Q. No. 'm'	Spin Q. No. 's'	No. of electrons on a subshell	No. of electrons on a main shell
1	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
	1(p)	−1	$+\frac{1}{2}, -\frac{1}{2}$		8
		0	$+\frac{1}{2}, -\frac{1}{2}$	6	
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
3	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
		−1	$+\frac{1}{2}, -\frac{1}{2}$		
	1(p)	0	$+\frac{1}{2}, -\frac{1}{2}$	6	
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
		−2	$+\frac{1}{2}, -\frac{1}{2}$		18
		−1	$+\frac{1}{2}, -\frac{1}{2}$		
	2(d)	0	$+\frac{1}{2}, -\frac{1}{2}$	10	
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
		+2	$+\frac{1}{2}, -\frac{1}{2}$		
4	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
	1(p)			6	
	2(d)			10	
		−3	$+\frac{1}{2}, -\frac{1}{2}$		
		−2	$+\frac{1}{2}, -\frac{1}{2}$		
		−1	$+\frac{1}{2}, -\frac{1}{2}$		32
	3(f)	0	$+\frac{1}{2}, -\frac{1}{2}$	14	
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
		+2	$+\frac{1}{2}, -\frac{1}{2}$		
		+3	$+\frac{1}{2}, -\frac{1}{2}$		

Conclusions:

(i) The maximum capacity of a main energy shell is equal to $2n^2$ electrons.

(ii) The maximum capacity of a subshell is equal to $2(2l+1)$ electrons.

Subenergy shell	Azimuthal Q. No. 'l'	Maximum capacity of electrons $2(2l+1)$
s	0	$2(2\times0+1)=2$
p	1	$2(2\times1+1)=6$
d	2	$2(2\times2+1)=10$
f	3	$2(2\times3+1)=14$

(iii) Number of subshells in a main energy shell is equal to the value of n.

Value of n	No. of subenergy shells	Designated as
1	1	$1s$
2	2	$2s, 2p$
3	3	$3s, 3p, 3d$
4	4	$4s, 4p, 4d, 4f$

(iv) Number of orbitals in a main energy shell is equal to n^2.

n	No. of orbitals	
1	$(1)^2=1$	s
2	$(2)^2=4$	s, p_x, p_y, p_z
3	$(3)^2=9$	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$

(v) One orbital cannot have more than two electrons. If two electrons are present, their spins should be in opposite directions.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

23. The orbital angular momentum of an electron in a d-orbital is: **(DCE 2007)**

(a) $\sqrt{6}\,\frac{h}{2\pi}$ (b) $\sqrt{2}\,\frac{h}{2\pi}$ (c) $\frac{h}{2\pi}$ (d) $\frac{2h}{2\pi}$

[Ans. (a)]

[**Hint:** Orbital angular momentum $= \sqrt{l(l+1)}\,\frac{h}{2\pi}$

$$= \sqrt{2(2+1)}\,\frac{h}{2\pi} = \sqrt{6}\,\frac{h}{2\pi}$$

(Here, $l = 2$, for d-orbitals)]

24. Which of the following sets of quantum numbers is correct for an electron in $4f$-orbital?

(Jamia Millia Islamia Engg. Ent. 2007)

(a) $n = 4, l = 3, m = +4, s = +\frac{1}{2}$
(b) $n = 4, l = 4, m = -4, s = -\frac{1}{2}$
(c) $n = 4, l = 3, m = +1, s = +\frac{1}{2}$
(d) $n = 3, l = 2, m = -2, s = +\frac{1}{2}$

[**Ans.** (c)]

[**Hint:** For $4f$, $n = 4, l = 3, m = -3, -2, -1, 0, +1, +2, +3$
$s = -\frac{1}{2}$ or $+\frac{1}{2}$]

25. Match the List-I with List-II and select the correct set from the following sets given below:

List-I	List-II
(A) The number of sub-energy levels in an energy level	(1) n^2
(B) The number of orbitals in a sub-energy level	(2) $3d$
(C) The number of orbitals in an energy level	(3) $2l + 1$
(D) $n = 3, l = 2, m = 0$	(4) n

[PET (Raj.) 2005]

Sets	(A)	(B)	(C)	(D)
(a)	4	3	1	2
(b)	3	1	2	4
(c)	1	2	3	4
(d)	3	4	1	2

[**Ans.** (a)]

[**Hint:** Number of orbitals in a shell $= n^2$

Number of subshells in a shell $= n$

Number of orbitals in a subshell $= (2l + 1)$

$n = 3, l = 2, m = 0$ represents $3d$]

26. Which of the following is not possible?

[BCECE (Medical) 2007]

(a) $n = 2, l = 1, m = 0$ (b) $n = 2, l = 0, m = -1$
(c) $n = 3, l = 0, m = 0$ (d) $n = 3, l = 1, m = -1$

[**Ans.** (b)]

[**Hint:** When $l = 0$, 'm' will also be equal to zero.]

27. What is the maximum number of electrons in an atom that can have the quantum numbers $n = 4$, $m_e = +1$?

[PMT (Kerala) 2007]

(a) 4 (b) 15 (c) 3 (d) 1 (e) 6

[**Ans.** (e)]

[**Hint:** $n = 4$; $l = 0$; $m_e = 0$
$l = 1$; $m_e = -1, 0, +1$
$l = 2$; $m_e = -2, -1, 0, +1, +2$
$l = 3$; $m_e = -3, -2, -1, 0, +1, +2, +3$

There are three orbitals having $m_e = +1$, thus maximum number of electrons in them will be 6.]

2.18 AUFBAU PRINCIPLE

Aufbau is a German word meaning 'building up'. This gives us a sequence in which various subshells are filled up depending on the relative order of the energy of the subshells. **The subshell with minimum energy is filled up first and when this obtains maximum quota of electrons, then the next subshell of higher energy starts filling.**

The sequence in which the various subshells are filled is the following:

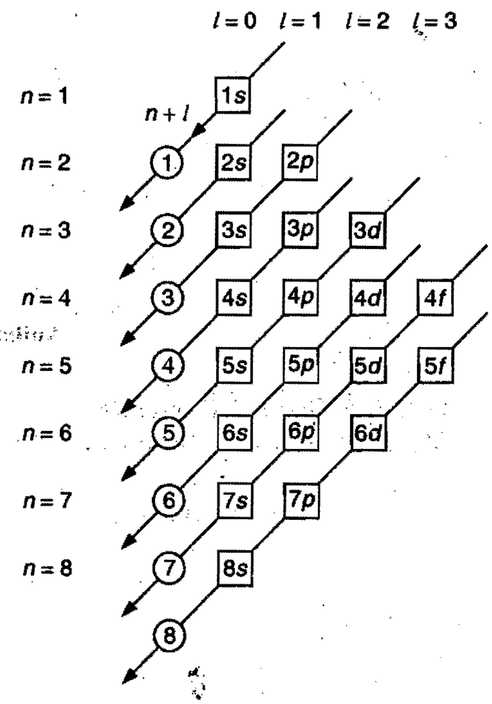


Fig. 2.18 Order of filling of various subshells

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p$.

The sequence in which various subshells are filled up can also be determined with the help of $(n + l)$ value for a given subshell. **The subshell with lowest $(n + l)$ value is filled up first. When two or more subshells have same $(n + l)$ value, the subshell with lowest value of 'n' is filled up first.**

Subshell	n	l	$(n + l)$	
$1s$	1	0	1	
$2s$	2	0	2	
$2p$	2	1	3	Lowest value of n
$3s$	3	0	3	
$3p$	3	1	4	Lowest value of n
$4s$	4	0	4	
$3d$	3	2	5	
$4p$	4	1	5	Lowest value of n
$5s$	5	0	5	

Subshell	n	l	$(n+l)$	
$4d$	4	2	6	
$5p$	5	1	6	Lowest value of n
$6s$	6	0	6	
$4f$	4	3	7	
$5d$	5	2	7	Lowest value of n
$6p$	6	1	7	
$7s$	7	0	7	
$5f$	5	3	8	
$6d$	6	2	8	Lowest value of n
$7p$	7	1	8	

The energy of electron in a hydrogen atom and other single electron species like He^+, Li^{2+} and Be^{3+} is determined solely by the principal quantum number. The energy of orbitals in hydrogen and hydrogen like species increases as follows:

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \ldots$$

The complete electronic configuration of all the known elements have been given in the table on next page. It is observed that few of the elements possess slightly different electronic configurations than expected on the basis of **Aufbau Principle.** These elements have been marked with asterisk (*) sign.

2.19 HUND'S RULE OF MAXIMUM MULTIPLICITY (Orbital Diagrams)

There is one more method of representing the electronic configuration which is usually called as **orbital diagram.** In this method, the electron is shown by an arrow: upward direction $\uparrow$ (clockwise spin) and downward direction $\downarrow$ (anti-clockwise spin).

To indicate the distribution of electrons among the orbitals of an atom, arrows are placed over bars that symbolise orbitals.

Hydrogen, for example, is represented as $\frac{\uparrow}{1s}$. The next element with atomic number 2 is helium. It is represented as $\frac{\uparrow\downarrow}{1s}$, *i.e.*, both the electrons are present on the same orbital 1s and are paired (spins are in opposite directions). The next two elements are Li and Be with three and four electrons, respectively. These are represented by orbital diagrams as:

Li $\quad \frac{\uparrow\downarrow}{1s}\ \frac{\uparrow}{2s}$

Be $\quad \frac{\uparrow\downarrow}{1s}\ \frac{\uparrow\downarrow}{2s}$

These can also be written as:

Li $\quad [He]\frac{\uparrow}{2s}$

Be $\quad [He]\frac{\uparrow\downarrow}{2s}$

In Be, 2s-orbital has been completed. The fifth electron in the case of boron enters the next available subshell which is $2p$. Thus, the electronic configuration of boron is $1s^2 2s^2 2p^1$. In the orbital diagram $[He]\frac{\uparrow\downarrow}{2s} - \frac{\uparrow}{2p} -$, the $2p$ subshell has three orbitals p_x, p_y and p_z. All the three have same energy. The electron can be accommodated on any one of the 2p-orbitals. In the case of carbon, sixth electron is also accommodated on $2p$ subshell and its electronic configuration is represented as $1s^2 2s^2 2p^2$ but three orbital diagrams can be expected.

(i) $[He]\frac{\uparrow\downarrow}{2s}\ \underbrace{\frac{\uparrow}{}\ \frac{\uparrow}{}\ \frac{}{}}_{2p}$ Electrons are present on two different orbitals with parallel spins.

(ii) $[He]\frac{\uparrow\downarrow}{2s}\ \underbrace{\frac{\uparrow}{}\ \frac{\downarrow}{}\ \frac{}{}}_{2p}$ Electrons are present on two different orbitals with opposite spins.

(iii) $[He]\frac{\uparrow\downarrow}{}\ \underbrace{\frac{\uparrow\downarrow}{}\ \frac{}{}\ \frac{}{}}_{2p}$ Both the electrons are present on one orbital with opposite spins.

Experiments show that (i) orbital diagram is correct while (ii) and (iii) are not correct. This has given birth to a new rule known as **Hund's rule of maximum multiplicity.** It states that **electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons with parallel spins.** Thus, the orbitals available in a subshell are first filled singly before they begin to pair. This means that pairing of electrons occurs with the introduction of second electron in s-orbitals, the fourth electron in p-orbitals, sixth electron in d-orbitals and eighth electron in f-orbitals. The orbital diagrams of nitrogen, oxygen, fluorine and neon are as given below:

Nitrogen	(7)	[He]	$\frac{\uparrow\downarrow}{2s}\ \underbrace{\frac{\uparrow}{}\ \frac{\uparrow}{}\ \frac{\uparrow}{}}_{2p}$
Oxygen	(8)	[He]	$\frac{\uparrow\downarrow}{2s}\ \underbrace{\frac{\uparrow\downarrow}{}\ \frac{\uparrow}{}\ \frac{\uparrow}{}}_{2p}$
Fluorine	(9)	[He]	$\frac{\uparrow\downarrow}{2s}\ \underbrace{\frac{\uparrow\downarrow}{}\ \frac{\uparrow\downarrow}{}\ \frac{\uparrow}{}}_{2p}$
Neon	(10)	[He]	$\frac{\uparrow\downarrow}{2s}\ \underbrace{\frac{\uparrow\downarrow}{}\ \frac{\uparrow\downarrow}{}\ \frac{\uparrow\downarrow}{}}_{2p}$

The orbital diagrams of elements from atomic number 21 to 30 can be represented on similar lines as below:

		3d	3d	3d	3d	3d	4s
Sc	$[Ar]\,3d^1 4s^2$ [Ar]	$\uparrow$	—	—	—	—	$\uparrow\downarrow$
Ti	$[Ar]\,3d^2 4s^2$	$\uparrow$	$\uparrow$	—	—	—	$\uparrow\downarrow$
V	$[Ar]\,3d^3 4s^2$	$\uparrow$	$\uparrow$	$\uparrow$	—	—	$\uparrow\downarrow$
Cr	$[Ar]\,3d^5 4s^1$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
Mn	$[Ar]\,3d^5 4s^2$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Fe	$[Ar]\,3d^6 4s^2$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Co	$[Ar]\,3d^7 4s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Ni	$[Ar]\,3d^8 4s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Cu	$[Ar]\,3d^{10} 4s^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$
Zn	$[Ar]\,3d^{10} 4s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

ELECTRONIC CONFIGURATION OF ELEMENTS

Element	At. No.	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s 5p 5d 5f
H	1	1										
He	2	2										(1s completed)
Li	3	2	1									
Be	4	2	2									(2s completed)
B	5	2	2	1								
C	6	2	2	2								
N	7	2	2	3								
O	8	2	2	4								
F	9	2	2	5								
Ne	10	2	2	6								(2p completed)
Na	11	2	2	6	1							
Mg	12	2	2	6	2							(3s completed)
Al	13	2	2	6	2	1						
Si	14	2	2	6	2	2						
P	15	2	2	6	2	3						
S	16	2	2	6	2	4						
Cl	17	2	2	6	2	5						
Ar	18	2	2	6	2	6						(3p completed)
K	19	2	2	6	2	6		1				
Ca	20	2	2	6	2	6		2				(4s completed)
Sc	21	2	2	6	2	6	1	2				
Ti	22	2	2	6	2	6	2	2				
V	23	2	2	6	2	6	3	2				
*Cr	24	2	2	6	2	6	5	1				
Mn	25	2	2	6	2	6	5	2				
Fe	26	2	2	6	2	6	6	2				
Co	27	2	2	6	2	6	7	2				
Ni	28	2	2	6	2	6	8	2				
*Cu	29	2	2	6	2	6	10	1				
Zn	30	2	2	6	2	6	10	2				(3d completed)
Ga	31	2	2	6	2	6	10	2	1			
Ge	32	2	2	6	2	6	10	2	2			
As	33	2	2	6	2	6	10	2	3			
Se	34	2	2	6	2	6	10	2	4			
Br	35	2	2	6	2	6	10	2	5			
Kr	36	2	2	6	2	6	10	2	6			(4p completed)
Rb	37	2	2	6	2	6	10	2	6			1
Sr	38	2	2	6	2	6	10	2	6			2 (5s completed)
Y	39	2	2	6	2	6	10	2	6	1		2
Zr	40	2	2	6	2	6	10	2	6	2		2
*Nb	41	2	2	6	2	6	10	2	6	4		1
*Mo	42	2	2	6	2	6	10	2	6	5		1
Tc	43	2	2	6	2	6	10	2	6	5		2
*Ru	44	2	2	6	2	6	10	2	6	7		1
*Rh	45	2	2	6	2	6	10	2	6	8		1
*Pd	46	2	2	6	2	6	10	2	6	10		
*Ag	47	2	2	6	2	6	10	2	6	10		1
Cd	48	2	2	6	2	6	10	2	6	10		2 (4d completed)
In	49	2	2	6	2	6	10	2	6	10		2 1
Sn	50	2	2	6	2	6	10	2	6	10		2 2
Sb	51	2	2	6	2	6	10	2	6	10		2 3
Te	52	2	2	6	2	6	10	2	6	10		2 4
I	53	2	2	6	2	6	10	2	6	10		2 5
Xe	54	2	2	6	2	6	10	2	6	10		2 6 (5p completed)

ELECTRONIC CONFIGURATION OF ELEMENTS

Element	At. No.	K	L	M	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s
Cs	55	2	8	18	2	6	10		2	6			1				
Ba	56	2	8	18	2	6	10		2	6			2	(6s completed)			
*La	57	2	8	18	2	6	10		2	6	1		2				
*Ce	58	2	8	18	2	6	10	1	2	6	1		2				
Pr	59	2	8	18	2	6	10	3	2	6			2				
Nd	60	2	8	18	2	6	10	4	2	6			2				
*Pm	61	2	8	18	2	6	10	5	2	6			2				
Sm	62	2	8	18	2	6	10	6	2	6			2				
Eu	63	2	8	18	2	6	10	7	2	6			2				
*Gd	64	2	8	18	2	6	10	7	2	6	1		2				
Tb	65	2	8	18	2	6	10	9	2	6			2				
Dy	66	2	8	18	2	6	10	10	2	6			2				
Ho	67	2	8	18	2	6	10	11	2	6			2				
Er	68	2	8	18	2	6	10	12	2	6			2				
Tm	69	2	8	18	2	6	10	13	2	6			2				
Yb	70	2	8	18	2	6	10	14	2	6			2				
Lu	71	2	8	18	2	6	10	14	2	6	1		2	(4f completed)			
Hf	72	2	8	18	32				2	6	2		2				
Ta	73	2	8	18	32				2	6	3		2				
W	74	2	8	18	32				2	6	4		2				
Re	75	2	8	18	32				2	6	5		2				
Os	76	2	8	18	32				2	6	6		2				
Ir	77	2	8	18	32				2	6	7		2				
*Pt	78	2	8	18	32				2	6	9		1				
*Au	79	2	8	18	32				2	6	10		1				
Hg	80	2	8	18	32				2	6	10		2	(5d completed)			
Tl	81	2	8	18	32				2	6	10		2	1			
Pb	82	2	8	18	32				2	6	10		2	2			
Bi	83	2	8	18	32				2	6	10		2	3			
Po	84	2	8	18	32				2	6	10		2	4			
At	85	2	8	18	32				2	6	10		2	5			
Rn	86	2	8	18	32				2	6	10		2	6(6p completed)			
Fr	87	2	8	18	32				2	6	10		2	6			1
Ra	88	2	8	18	32				2	6	10		2	6			2 (7s completed)
*Ac	89	2	8	18	32				2	6	10		2	6	1		2
*Th	90	2	8	18	32				2	6	10	0	2	6	2		2
*Pa	91	2	8	18	32				2	6	10	2	2	6	1		2
*U	92	2	8	18	32				2	6	10	3	2	6	1		2
*Np	93	2	8	18	32				2	6	10	4	2	6	1		2
Pu	94	2	8	18	32				2	6	10	6	2	6			2
Am	95	2	8	18	32				2	6	10	7	2	6			2
*Cm	96	2	8	18	32				2	6	10	7	2	6	1		2
*Bk	97	2	8	18	32				2	6	10	8	2	6	1		2
Cf	98	2	8	18	32				2	6	10	10	2	6			2
Es	99	2	8	18	32				2	6	10	11	2	6			2
Fm	100	2	8	18	32				2	6	10	12	2	6			2
Md	101	2	8	18	32				2	6	10	13	2	6			2
No	102	2	8	18	32				2	6	10	14	2	6			2
*Lr	103	2	8	18	32				2	6	10	14	2	6	1		2 (5f completed)
Ku or Rf	104	2	8	18	32				2	6	10	14	2	6	2		2
Ha or Db	105	2	8	18	32				2	6	10	14	2	6	3		2
Sg	106	2	8	18	32				2	6	10	14	2	6	4		2
Bh	107	2	8	18	32				2	6	10	14	2	6	5		2 Predicted electronic configurations
Hs	108	2	8	18	32				2	6	10	14	2	6	6		2
Mt	109	2	8	18	32				2	6	10	14	2	6	7		2
*Uun or Ds	110	2	8	18	32				2	6	10	14	2	6	9		1
*Uuu or Rg	111	2	8	18	32				2	6	10	14	2	6	10		1
Uub	112	2	8	18	32				2	6	10	14	2	6	10		2 (6d completed)

All those atoms which consist of at least one of the orbitals singly occupied behave as **paramagnetic** materials because these are weakly attracted to a magnetic field, while all those atoms in which all the orbitals are doubly occupied behave as **diamagnetic** materials because they have no attraction for magnetic field. However, these are slightly repelled by magnetic field due to induction.

Magnetic moment may be calculated as,

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

$$1\ \text{BM (Bohr Magneton)} = \frac{eh}{4\pi mc}$$

where, n = no. of unpaired electron

Exceptions to Aufbau Principle

In some cases, it is seen that actual electronic arrangement is slightly different from arrangement given by aufbau principle. A simple reason behind this is that half-filled and full-filled subshells have got extra stability.

Cr_{24}	$\longrightarrow$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4, 4s^2$	(wrong)
	$\longrightarrow$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$	(right)
Cu_{29}	$\longrightarrow$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$	(wrong)
	$\longrightarrow$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$	(right)

Similarly the following elements have slightly different configurations than expected:

$$Nb_{41} \longrightarrow [Kr]4d^4 5s^1$$
$$Mo_{42} \longrightarrow [Kr]4d^5 5s^1$$
$$Ru_{44} \longrightarrow [Kr]4d^7 5s^1$$
$$Rh_{45} \longrightarrow [Kr]4d^8 5s^1$$
$$Pd_{46} \longrightarrow [Kr]4d^{10} 5s^0$$
$$Ag_{47} \longrightarrow [Kr]4d^{10} 5s^1$$
$$Pt_{78} \longrightarrow [Xe]4f^{14} 5d^9 6s^1$$
$$Au_{79} \longrightarrow [Xe]4f^{14} 5d^{10} 6s^1$$
$$La_{57} \longrightarrow [Kr]\,4d^{10} 5s^2 5p^6 5d^1 6s^2$$
$$Ce_{58} \longrightarrow [Kr]\,4d^{10} 4f^2 5s^2 5p^6 5d^0 6s^2$$
$$Gd_{64} \longrightarrow [Kr]\,4d^{10} 4f^7 5s^2 5p^6 5d^1 6s^2$$

2.20 PHOTOELECTRIC EFFECT

Emission of electrons from a metal surface when exposed to light radiations of appropriate wavelength is called **photoelectric effect**. The emitted electrons are called **photoelectrons**.

Work function or threshold energy may be defined as the minimum amount of energy required to eject electrons from a metal surface.

According to Einstein,

Maximum kinetic energy of the ejected electron

= absorbed energy − work function

$$\frac{1}{2} mv^2_{\max} = h\nu - h\nu_0$$

$$= hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$$

where, ν_0 and λ_0 are threshold frequency and threshold wavelength respectively.

Stopping potential: The minimum potential at which the plate photoelectric current becomes zero is called **stopping potential.**

If V_0 is the stopping potential, then

$$eV_0 = h(\nu - \nu_0)$$

Laws of Photoelectric Effect

(i) Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.

(ii) The maximum kinetic energy of photoelectrons is directly proportional to the frequency of incident radiation; moreover, it is independent of the intensity of light used.

(iii) There is no time lag between incidence of light and emission of photoelectrons.

(iv) For emission of photoelectrons, the frequency of incident light must be equal to or greater than the threshold frequency.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

28. The maximum kinetic energy of photoelectrons ejected from a metal, when it is irradiated with radiation of frequency $2 \times 10^{14}\ s^{-1}$ is 6.63×10^{-20} J. The threshold frequency of the metal is: [PMT (Kerala) 2008]

(a) $2 \times 10^{14}\ s^{-1}$ (b) $3 \times 10^{14}\ s^{-1}$
(c) $2 \times 10^{-14}\ s^{-1}$ (d) $1 \times 10^{-14}\ s^{-1}$
(e) $1 \times 10^{14}\ s^{-1}$

[Ans. (e)]

[Hint : Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$h\nu = h\nu_0 + \text{KE}$$
$$h\nu_0 = h\nu - \text{KE}$$
$$6.626 \times 10^{-34} \times \nu_0 = 6.626 \times 10^{-34} \times 2 \times 10^{14} - 6.63 \times 10^{-20}$$
$$\nu_0 = \frac{1.3252 \times 10^{-19} - 6.63 \times 10^{-20}}{6.626 \times 10^{-34}}$$
$$\nu_0 = 9.99 \times 10^{13} = 10^{14}\ s^{-1}\ ]$$

29. If λ_0 and λ be the threshold wavelength and the wavelength of incident light, the velocity of photoelectrons ejected will be:

(a) $\sqrt{\frac{2h}{m}(\lambda_0 - \lambda)}$ (b) $\sqrt{\frac{2hc}{m}(\lambda_0 - \lambda)}$
(c) $\sqrt{\frac{2hc}{m}\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right)}$ (d) $\sqrt{\frac{2h}{m}\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right)}$

[Ans. (c)]

[Hint : Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \frac{1}{2}mv^2$$

$$v = \sqrt{\frac{2hc}{m}\frac{(\lambda_0 - \lambda)}{\lambda\lambda_0}}]$$

30. A radiation of wavelength λ illuminates a metal and ejects photoelectrons of maximum kinetic energy of 1eV. Another radiation of wavelength $\frac{\lambda}{3}$, ejects photoelectrons of maximum kinetic energy of 4 eV. What will be the work function of metal?
(a) 1eV (b) 2eV (3) 0.5eV (d) 3eV
[Ans. (c)]
[Hint : Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$h\frac{c}{\lambda} = E_0 + 1\text{ eV} \quad ...(i)$$

$$3h\frac{c}{\lambda} = E_0 + 4\text{eV} \quad ...(ii)$$

$$3(E_0 + 1\text{ eV}) = E_0 + 4\text{eV}$$

$$E_0 = 0.5\text{eV}]$$

31. The ratio of slopes of maximum kinetic energy *versus* frequency and stopping potential (V_0) *versus* frequency, in photoelectric effect gives:
(a) charge of electron (b) planck's constant
(c) work function (d) threshold frequency
[Ans. (a)]
[Hint :

$$h\nu = h\nu_0 + eV_0$$

$$eV_0 = h\nu - h\nu_0$$

$$V_0 = \frac{h}{e}\nu - \frac{h}{e}\nu_0 \quad ...(i)$$

$$(\text{Slope})_1 = h/e$$

$$(\text{KE})_{max} = h\nu - h\nu_0 \quad ...(ii)$$

$$(\text{Slope})_2 = h$$

$$(\text{Slope})_2/(\text{Slope})_1 = \frac{h}{h/e} = e]$$

32. Ground state energy of H-atom is $(-E_1)$, the velocity of photoelectrons emitted when photon of energy E_2 strikes stationary Li^{2+} ion in ground state will be:
(a) $v = \sqrt{\frac{2(E_2 - E_1)}{m}}$ (b) $v = \sqrt{\frac{2(E_2 + 9E_1)}{m}}$
(c) $v = \sqrt{\frac{2(E_2 - 9E_1)}{m}}$ (d) $v = \sqrt{\frac{2(E_2 - 3E_1)}{m}}$
[Ans. (c)]
[Hint: Threshold energy of $Li^{2+} = 9E_1$
Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$E_2 = 9E_1 + \frac{1}{2}mv^2$$

$$mv^2 = 2(E_2 - 9E_1)$$

$$v = \sqrt{\frac{2(E_2 - 9E_1)}{m}}]$$

2.21 SOME OTHER FUNDAMENTAL PARTICLES

Besides protons, neutrons and electrons, many more elementary particles have been discovered. These particles are also called **Fundamental particles.** Some of these particles are stable while the others are unstable. Out of stable particles, the electron, the proton, the antiproton and the positron are four mass particles while neutrino, photon and graviton are three energy particles. Among these, unstable particles are neutron, meson and ν-particles. The main characteristics of the particles are given in table 2.1 below.

Table 2.1

Particle	Symbol	Nature	Charge esu × 10^{-10}	Mass (amu)	Discovered by
Positron	e^+, $1e^0$, β^+	+	+ 4.8029	0.0005486	Anderson (1932)
Neutrino	ν	0	0	< 0.00002	Pauli
Antiproton	p^-	–	– 4.8029	1.00787	Chamberlain Sugri and Weighland (1955)
Photon	$h\nu$	0	0	0	Planck
Graviton	G	0	0	0	
Positive mu meson	μ^+	+	+ 4.8029	0.1152	Yukawa (1935)
Negative mu meson	μ^-	–	– 4.8029	0.1152	Anderson (1937)
Positive pi meson	π^+	+	+ 4.8029	0.1514	Powell (1947)
Negative pi meson	π^-	–	– 4.8029	0.1514	
Neutral pi meson	π^0	0	0	0.1454	

2.22 ISOTOPES

Isotopes are the atoms of the same element having different atomic masses (see determination of isotopic mass). The term 'isotope' was introduced by **Soddy**. This is a Greek word meaning same position (*Isos* = same, *topes* = position), since all the isotopes of an element occupy the same position in the periodic table. Isotopes of an element possess identical chemical properties but differ slightly in physical properties which depend on atomic mass. Isotopes were first identified in radioactive elements by **Soddy**. In 1919, Thomson established the existence of isotopes in a non-radioactive element, neon. Until now, more than 1000 isotopes have been identified (natural as well as artificial). Out of these about 320 occur in nature, approximately 280 of these are stable and the remaining 40 are radioactive.

Conclusions

(i) Number of neutrons present in the nuclei of various isotopes of an element is always different. The number of neutrons is determined by applying the formula $N = A - Z$ where A is mass number and Z is atomic number.
Hydrogen has three isotopes, ${}_1^1H$, ${}_1^2H$ and ${}_1^3H$.

	A (Mass number)	Z	No. of neutrons
${}_1^1H$	1	1	0
${}_1^2H$	2	1	1
${}_1^3H$	3	1	2

Oxygen has three isotopes, ${}^{16}O$, ${}^{17}O$ and ${}^{18}O$.

	A	Z	No. of neutrons
${}_8^{16}O$	16	8	8
${}_8^{17}O$	17	8	9
${}_8^{18}O$	18	8	10

(ii) In a neutral atom, the number of protons and the number of electrons are always the same, *i.e.*, the electronic configuration of all the isotopes of an element is the same. Thus, all the isotopes of an element show the same chemical properties. However, the rates of reactions may be different for different isotopes of an element.

(iii) All the isotopes of an element occupy the same position in the periodic table.

(iv) The isotopes of an element differ slightly in physical properties. The compounds formed by these isotopes will also have different physical properties.

Determination of Isotopic Mass

Chlorine has two isotopes ${}_{17}Cl^{35}$ and ${}_{17}Cl^{37}$; these are found in nature in 3 : 1 ratio or 75% : 25% respectively. Isotopic mass may be calculated as:

Isotopic mass of chlorine

$$= \frac{\%\text{ of } Cl^{35}}{100} \times \text{mass of } Cl^{35} + \frac{\%\text{ of } Cl^{37}}{100} \times \text{mass of } Cl^{37}$$

$$= \frac{75}{100} \times 35 + \frac{25}{100} \times 37 = 35.5$$

OR

Isotopic mass of chlorine

$$= \frac{\text{Ratio of } Cl^{35} \times \text{mass of } Cl^{35} + \text{Ratio of } Cl^{37} \times \text{mass of } Cl^{37}}{\text{Sum of ratio}}$$

$$= \frac{3 \times 35 + 1 \times 37}{4} = 35.5$$

2.23 THEORIES OF NUCLEAR STABILITY

Since, a nucleus contains positively charged protons, there must exist a strong repulsive force between them. It has been calculated that there exists an electrostatic repulsion of approximately six tons between two protons situated at a nuclear distance but at the same time the forces which bind the nucleus are very high. It has been found that nuclear forces attracting the same two particles (*i.e.*, protons) are at least forty times greater than the repulsive forces. Thus, two major forces exist in the nucleus. These are electrostatic and nuclear. The nuclear forces are stronger and the range of these forces is extremely small. The forces which operate between nucleons are referred to as exchange forces. In order to account for the stability of the nucleus, a theory known as **meson theory** was put forward by **Yukawa,** in 1935. Yukawa pointed out that neutrons and protons are held together by very rapid exchange of nuclear particles called **pi mesons.** These mesons may be electrically neutral, positive or negative (designated as π^0, π^+ and π^-) and possess a mass 275 times the mass of an electron. Nuclear forces arise from a constant exchange of mesons between nucleons with very high velocity (practically the velocity of light).

Let a neutron be converted into a proton by the emission of a negative meson. The emitted meson is accepted by another proton and converted into a neutron.

$$n_A \rightarrow p_A^+ + \pi^-$$
$$\pi^- + p_B^+ \rightarrow n_B$$

Similarly, a proton after emitting a positive meson is converted into a neutron and *vice-versa.*

$$p_A^+ \rightarrow n_A + \pi^+$$
$$\pi^+ + n_B \rightarrow p_B^+$$

or simply
$$p \rightleftharpoons \pi^+ + n$$
$$n \rightleftharpoons \pi^- + p$$

There may be two more types of exchange, *i.e.*, between neutron-neutron and proton-proton, involving neutral pi mesons.

$$\begin{matrix} p \searrow \\ p \swarrow \end{matrix} \pi^0 \quad \begin{matrix} n \searrow \\ n \swarrow \end{matrix} \pi^0 \quad \text{or simply} \quad p \underset{\pi^0}{\overset{\pi^0}{\rightleftharpoons}} p \quad \text{and} \quad n \underset{\pi^0}{\overset{\pi^0}{\rightleftharpoons}} n$$

Mass Defect—Binding Energy

It is observed that the atomic mass of all nuclei (except hydrogen) is different from the sum of the masses of protons and neutrons. For example, the helium nucleus consists of 2 protons and 2 neutrons. The combined mass of 2 protons and 2 neutrons should be

$$= 2 \times 1.00758 + 2 \times 1.00893$$
$$= 4.03302 \text{ amu}$$

The actual observed mass of helium nuclei is 4.0028 amu. A difference of 0.0302 amu is observed between these two values. This difference is termed as **mass defect.**

$$\text{Mass defect} = \text{Total mass of nucleons} - \text{Observed atomic mass}$$

This decrease in mass (*i.e.*, mass defect) is converted into energy according to Einstein equation $E = mc^2$. The energy released when a nucleus is formed from protons and neutrons is called the **binding energy.** This is the force which holds all the nucleons together in the nucleus. Binding energy can be defined in other ways also, *i.e.*, the energy required to break the nucleus into constituent protons and neutrons. Binding energy is measured in MeV (Million Electron-Volts), *i.e.*, 1 amu = 931 MeV.

$$\text{Binding energy} = \text{Mass defect} \times 931 \text{ MeV}$$

Binding energy can also be calculated in erg. This is

$$= \text{Mass defect (amu)} \times 1.66 \times 10^{-24} \times (3 \times 10^{10})^2 \text{ erg}$$

$$(1\,\text{MeV} = 1.60 \times 10^{6} \text{ erg})$$

The binding energy increases with the increase in atomic number of the element. This indicates that heavier nuclei should be more stable than lighter nuclei. But, it is not so because heavier nuclei above atomic number 82 are unstable. It is thus clear that total binding energy of a nucleus does not explain the stability of the nucleus.

The total binding energy of a nucleus when divided by the number of nucleons gives the average or mean binding energy per nucleon. The binding energy per nucleon is actually the measure of the stability of the nucleus. The greater the binding energy per nucleon, more stable is the nucleus.

$$\text{Binding energy per nucleon} = \frac{\text{Total binding energy}}{\text{Total number of nucleons}}$$

When binding energy per nucleon of a number of nuclei is plotted against the corresponding mass number, a graph is obtained (Fig. 2.19) whose characteristics are as follows:

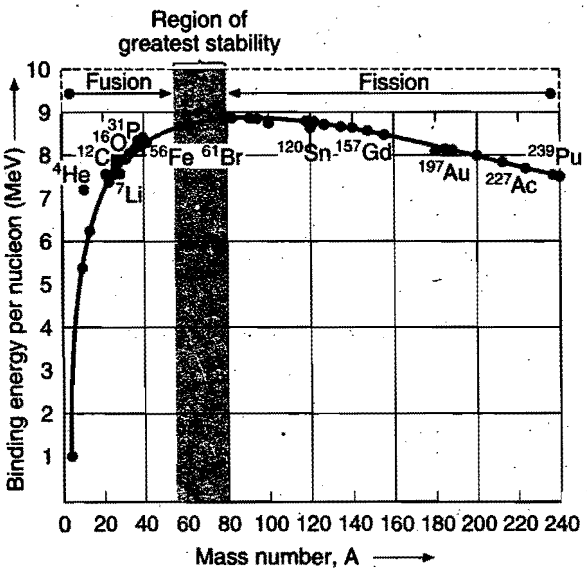


Fig. 2.19

(i) Binding energy per nucleon increases from 1.1 to 8.0 MeV from mass number 2 to 20.

(ii) Binding energy per nucleon increases from 8 to 8.6 MeV from mass number 20 to 40.

(iii) Binding energy per nucleon remains 8.6 – 8.7 MeV from mass number 40 to 90. Iron (56) has the maximum value of 8.7 MeV per nucleon.

(iv) The value of binding energy per nucleon decreases from 8.6 to 7.5 MeV from mass number 90 to 240.

(v) Points for helium, carbon, oxygen lie quite high in the graph showing that these nuclei are highly stable.

The binding energy per nucleon can be increased in two ways:

(i) Either by breaking heavy nucleus to those of intermediate mass numbers (process of fission) or

(ii) By fusing lighter nuclei to form heavier nuclei (process of fusion).

2.24 THE WHOLE NUMBER RULE AND PACKING FRACTION

Aston believed that mass number values (sum of protons and neutrons) of isotopes should be whole numbers on the scale of oxygen ($^{16}O = 16$) but actually it was observed that these were not integers. The difference in the atomic mass of an isotope and mass number was expressed by **Aston** (1927) as **packing fraction** by the following expression:

$$\text{Packing fraction} = \frac{\text{Isotopic atomic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

Thus, the packing fraction of $^{1}H = \frac{1.0078 - 1}{1} \times 10^4 = 78$ and the packing fraction of $^{35}Cl = \frac{34.980 - 35.0}{35.0} \times 10^4 = -5.7$. The packing fraction of oxygen is zero.

It is clear that the value of packing fraction varies from one atom to other. This is sometime positive or zero but more often negative.

A negative packing fraction means that atomic mass is less than nearest whole number and this suggests that some mass has been converted into energy when the particular isotope has been constituted. This energy is responsible for nuclear stability. All those having negative values of packing fraction are stable nuclei.

A positive packing fraction generally indicates instability of the nucleus. However, this statement is not correct for lighter nuclei.

In general, lower the value of packing fraction, the greater is the stability of the nucleus. The lowest values of packing fractions are observed for transition elements or iron family indicating thereby maximum stability of their nuclei.

2.25 THE MAGIC NUMBERS

It has been observed that atoms with an even number of nucleons in their nuclei are more plentiful than those with odd number. This indicates that a nucleus made up of even number of nucleons is more stable than a nuclei which consists of odd number of nucleons. It has also been observed that a stable nuclei results when either the number of neutrons or that of protons is equal to one of the numbers 2, 8, 20, 50, 82, 126. These numbers are called **magic numbers.** It is thought that the magic numbers form closed nuclear shells in the same way as the atomic numbers of inert gases form stable electronic configuration. In general, elements that have nuclei with magic number of protons as well as magic number of neutrons such as $^{4}_{2}He$, $^{16}_{8}O$, $^{40}_{20}Ca$, $^{208}_{82}Pb$ are highly stable and found in abundance in nature.

A survey of stable nuclei found in nature shows the following trend:

Protons	Even	Even	Odd	Odd
Neutrons	Even	Odd	Even	Odd
No. of stable nuclei	157	52	50	5

Only five stable odd-odd nuclides are known; these nuclides are $^{2}_{1}H$, $^{6}_{3}Li$, $^{10}_{5}B$, $^{14}_{7}N$ and $^{180}_{73}Ta$.

SOME SOLVED EXAMPLES

Example 46. *The minimum energy required to overcome the attractive forces between an electron and the surface of Ag metal is 5.52×10^{-19} J. What will be the maximum kinetic energy of electrons ejected out from Ag which is being exposed to UV light of $\lambda = 360$ Å?*

Solution: Energy of the photon absorbed

$$= \frac{h \cdot c}{\lambda} = \frac{6.625 \times 10^{-27} \times 3 \times 10^{10}}{360 \times 10^{-8}}$$

$$= 5.52 \times 10^{-11} \text{ erg}$$

$$= 5.52 \times 10^{-18} \text{ J}$$

$$E(\text{photon}) = \text{work function} + \text{KE}$$

$$\text{KE} = 5.52 \times 10^{-18} - 7.52 \times 10^{-19}$$

$$= 47.68 \times 10^{-19} \text{ J}$$

Example 47. *Let a light of wavelength λ and intensity 'I' strikes a metal surface to emit x electrons per second. Average energy of each electron is 'y' unit. What will happen to 'x' and 'y' when (a) λ is halved (b) intensity I is doubled?*

Solution: (a) Rate of emission of electron is independent of wavelength. Hence, 'x' will be unaffected.

Kinetic energy of photoelectron = Absorbed energy − Threshold energy

$$y = \frac{hc}{\lambda} - w_0$$

when, λ is halved, average energy will increase but it will not become double.

(b) Rate of emission of electron per second 'x' will become double when intensity I is doubled. Average energy of ejected electron, *i.e.*, 'y' will be unaffected by increase in the intensity of light.

Example 48. *How many orbits, orbitals and electrons are there in an atom having atomic mass 24 and atomic number 12?*

Solution:

Atomic number = No. of protons = No. of electrons = 12

Electronic configuration = 2, 8, 2

No. of orbits = (K, L and M)

No. of orbitals on which electrons are present

= (one 1s + one 2s + three 2p + one 3s)

Example 49. *A neutral atom has 2K electrons, 8L electrons and 6 M electrons. Predict from this:*

(a) its atomic number, (b) total number of s-electrons, (c) total number of p-electrons, (d) total number of d-electrons.

Solution: (a) Total number of electrons

$$= (2 + 8 + 6) = 16$$

So, Atomic number = 16

Electronic configuration = $1s^2, 2s^2 2p^6, 3s^2 3p^4$

(b) Total number of s-electrons $= (1s^2 + 2s^2 + 3s^2) = 6$

(c) Total number of p-electrons $= (2p^6 + 3p^4) = 10$

(d) Total number of d-electrons = 0

Example 50. *Write down the values of quantum numbers of all the electrons present in the outermost orbit of argon (At. No. 18).*

Solution: The electronic configuration of argon is

$$1s^2, 2s^2 2p^6, 3s^2 3p_x^2 3p_y^2 3p_z^2$$

Values of quantum numbers are:

	n	l	m	s
$3s^2$	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$
$3p_x^2$	3	1	±1	$+\frac{1}{2}, -\frac{1}{2}$
$3p_y^2$	3	1	±1	$+\frac{1}{2}, -\frac{1}{2}$
$3p_z^2$	3	1	0	$+\frac{1}{2}, -\frac{1}{2}$

Example 51. *(a) An electron is in 5f-orbital. What possible values of quantum numbers n, l, m and s can it have?*

(b) What designation is given to an orbital having

(i) $n = 2, l = 1$ and (ii) $n = 3, l = 0$?

Solution: (a) For an electron in $5f$-orbital, quantum numbers are:

$$n = 5;\ l = 3;\quad m = -3, -2, -1, 0, +1, +2, +3$$

and $s = \text{either } +\frac{1}{2} \text{ or } -\frac{1}{2}$

(b) (i) $2p$, (ii) $3s$

Example 52. *Atomic number of sodium is 11. Write down the four quantum numbers of the electron having highest energy.*

Solution: The electronic configuration of sodium is:

$$1s^2, 2s^2 2p^6, 3s^1$$

$3s$-electron has the highest energy. Its quantum numbers are:

$$n = 3, l = 0, m = 0, s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

Example 53. *An element has 8 electrons in 4d-subshell. Show the distribution of 8 electrons in the d-orbitals of the element within small rectangles.*

Solution: $4d$-subshell has five d-orbitals. These are first occupied singly and then pairing occurs. The distribution can be shown in the following manner:

4d

↑↓	↑↓	↑↓	↑	↑

Example 54. *How many elements would be in the third period of the periodic table if the spin quantum number m_s could have the value $-\frac{1}{2}$, 0 and $+\frac{1}{2}$?*

Solution:

$n = 3, l = 0, m = 0$ $\qquad m_s = -\frac{1}{2}, 0, +\frac{1}{2}$

$l = 1;\ m = -1, 0, +1$ $\qquad m_s = -\frac{1}{2}, 0, +\frac{1}{2}$; $m_s = -\frac{1}{2}, 0, +\frac{1}{2}$; $m_s = -\frac{1}{2}, 0, +\frac{1}{2}$

$l = 2;\ m = -2, -1, 0, +1, +2$ $\qquad \left\{ m_s = -\frac{1}{2}, 0, +\frac{1}{2} \text{ for each value of magnetic quantum no.} \right\}$

Number of elements = $3s$ $(3e)$

$3p$ $(9e)$

$3d$ $(15e)$

$\therefore$ 27 elements will be there in third period of periodic table.

Example 55. *The binding energy of ^4_2He is 28.57 MeV. What shall be the binding energy per nucleon of this element?*

Solution: The nucleus of $^4_2$He consists of 4 nucleons.

$$\text{So, Binding energy per nucleon} = \frac{\text{Total binding energy}}{\text{No. of nucleons}}$$

$$= \frac{28.57}{4} = 7.14 \text{ MeV}$$

Example 56. *Calculate the binding energy of the oxygen isotope $^{16}_8O$. The mass of the isotope is 16.0 amu. (Given $e = 0.0005486$ amu, $p = 1.00757$ amu and $n = 1.00893$ amu.)*

Solution: The isotope $^{16}_8$O contains 8 protons, 8 neutrons and 8 electrons.

Actual mass of the nucleus of $^{16}_8$O

$$= 16 - \text{mass of 8 electrons}$$

$$= 16 - 8 \times 0.0005486 = 15.9956 \text{ amu}$$

Mass of the nucleus of $^{16}_8$O

$$= \text{mass of 8 protons} + \text{mass of 8 neutrons}$$

$$= 8 \times 1.00757 + 8 \times 1.00893 = 16.132 \text{ amu}$$

$$\text{Mass defect} = (16.132 - 15.9956) = 0.1364 \text{ amu}$$

$$\text{Binding energy} = 0.1364 \times 931 = 127 \text{ MeV}$$

Example 57. *There are four atoms which have mass numbers 9, 10, 11 and 12 respectively. Their binding energies are 54, 70, 66 and 78 MeV respectively. Which one of the atoms is most stable?*

Solution: Stability depends on the value of binding energy per nucleon.

	A	*B*	*C*	*D*
Binding energy (MeV)	54	70	66	78
No. of nucleons	9	10	11	12
Binding energy per nucleon (MeV)	6	7	6	6.5

Thus, *B* is most stable.

MISCELLANEOUS NUMERICAL EXAMPLES

These examples will give the sharp edge to the aspirants for IIT and various other entrance examinations.

Example 1. *The Schrödinger wave equation for hydrogen atom is*

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[2 - \frac{r_0}{a_0}\right]e^{-r/a_0}$$

where a_0 is Bohr radius. If the radial node in 2s be at r_0, then find r in terms of a_0. **(IIT 2004)**

Solution: Given,

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[2 - \frac{r_0}{a_0}\right]e^{-r/a_0}$$

$$\psi^2_{2s} = 0 \text{ at node}$$

$$\therefore \quad 2 - \frac{r_0}{a_0} = 0$$

$$r_0 = 2a_0$$

Example 2. *Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr radius) whose charge is neutralized by the addition of an electron to the cavity in vacuum infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralization process. Also, if the magnitude of average KE is half the magnitude of average potential energy, find the average potential energy.* **(IIT 1996)**

Solution:

Coulombic force of attraction = Centrifugal force

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze \times e}{a_0^2} = \frac{mv^2}{a_0}$$

where, v = velocity of electron

a_0 = distance between electron and nucleus

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a_0} = mv^2$$

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{2a_0}$$

$$\text{PE} = -2 \times \text{KE}$$

$$= -2 \times \frac{1}{4\pi\varepsilon_0} \times \frac{Ze^2}{2a_0} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a_0}$$

Example 3. *Hydrogen atoms are excited from ground state. Its spectrum contains wavelength 486 nm. Find, what transition does the line corresponds to. Also find from this information what other wavelengths will be present in the spectrum?*

Solution: Wavelength 486 nm, *i.e.*, 4860 Å indicates that the spectrum is in visible region, *i.e.*, Balmer series.

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{4860\times10^{-8}}=109677.76\times1^2\left[\frac{1}{2^2}-\frac{1}{n_2^2}\right]$$

On solving, we get

$$n_2^2=16$$

$$n_2=4$$

Thus, transition is from, $4\rightarrow2$

Other transitions in the spectrum are

$$4\rightarrow3\rightarrow2$$

$$\frac{1}{\lambda}=109677.76\times1^2\times\left[\frac{1}{3^2}-\frac{1}{4^2}\right]$$

$$\lambda=1875\times10^{-7}\text{ cm}$$

Example 4. *If uncertainties in the measurement of position and momentum of an electron are equal, calculate uncertainty in the measurement of velocity.*

Solution: According to Heisenberg's uncertainty principle,

$$\Delta x.\Delta p\geq\frac{h}{4\pi}$$

Given, $\Delta x=\Delta p=\sqrt{\frac{h}{4\pi}}=0.726\times10^{-17}$

$$\Delta p=m\,\Delta V$$

or $$\Delta V=\frac{\Delta p}{m}=\frac{0.726\times10^{-17}}{9.1\times10^{-31}}=7.98\times10^{12}\text{ ms}^{-1}$$

Example 5. *How much energy will be released when a sodium ion and a chloride ion, originally at infinite distance are brought together to a distance of 2.76 Å (the shortest distance of approach in a sodium chloride crystal)? Assume that ions act as point charges, each with a magnitude of 1.6×10^{-19} C. Permittivity constant of the medium is 9×10^9 Nm^2C^{-2}.*

Solution: Energy released

$$=-K\frac{q_1\,q_2}{r}=-\frac{9\times10^9\times(1.6\times10^{-19})^2}{2.76\times10^{-10}}=-8.35\times10^{-19}\text{ J}$$

Example 6. *The angular momentum of an electron in a Bohr orbit of H-atom is 4.2178×10^{-34} kg m^2/sec. Calculate the spectral line emitted when an electron falls from this level to the next lower level.*

Solution: We know, $mvr=n\frac{h}{2\pi}$

$$4.2178\times10^{-34}=n\times\frac{6.626\times10^{-34}}{2\times3.14}$$

$\therefore$ $$n=4$$

$$\frac{1}{\lambda}=R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$=109678\left[\frac{1}{3^2}-\frac{1}{4^2}\right]$$

$$\lambda=1.8\times10^{-4}\text{ cm}$$

Example 7. *A negatively charged particle called Negatron was discovered. In the Millikan's oil-drop experiment, the charges of the oil-drops in five experiments are reported as 3.2×10^{-19} coulomb; 4.8×10^{-19} coulomb; 6.4×10^{-19} coulomb; 8×10^{-19} coulomb and 9.6×10^{-19} coulomb. Calculate the charge on the negatron.*

Solution: In Millikan's oil-drop experiment; the charges on the oil-drops are integral multiples of the charge of the particle. Dividing the charges of droplets by the lowest charge:

(i) $\frac{3.2\times10^{-19}}{3.2\times10^{-19}}=1$ (ii) $\frac{4.8\times10^{-19}}{3.2\times10^{-19}}=1.5$

(iii) $\frac{6.4\times10^{-19}}{3.2\times10^{-19}}=2$ (iv) $\frac{8\times10^{-19}}{3.2\times10^{-19}}=2.5$

(v) $\frac{9.6\times10^{-19}}{3.2\times10^{-19}}=3$

All the values are not integral; they can be converted to integers on multiplying by 2.

$\therefore$ Charge of the negatron will be

$$\frac{3.2\times10^{-19}}{2}=1.6\times10^{-19}\text{ C}$$

Example 8. *When a certain metal was irradiated with light of frequency 3.2×10^{16} Hz, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 2.0×10^{16} Hz. Calculate ν_0 for the metal.*

Solution: Applying photoelectric equation,

$$\text{KE}=h\nu-h\nu_0$$

or $$(\nu-\nu_0)=\frac{\text{KE}}{h}$$

Given, $$\text{KE}_2=2\text{KE}_1$$

$$\nu_2-\nu_0=\frac{\text{KE}_2}{h}\quad\ldots\text{(i)}$$

and $$\nu_1-\nu_0=\frac{\text{KE}_1}{h}\quad\ldots\text{(ii)}$$

Dividing equation (i) by equation (ii),

$$\frac{\nu_2-\nu_0}{\nu_1-\nu_0}=\frac{\text{KE}_2}{\text{KE}_1}=\frac{2\text{KE}_1}{\text{KE}_1}=2$$

or $$\nu_2-\nu_0=2\nu_1-2\nu_0$$

or $$\nu_0=2\nu_1-\nu_2=2(2.0\times10^{16})-(3.2\times10^{16})$$

$$=8.0\times10^{15}\text{ Hz}$$

Example 9. *An electron moves in an electric field with a kinetic energy of 2.5 eV. What is the associated de Broglie wavelength?*

Solution: Kinetic energy

$$= \frac{1}{2} mv^2 \quad \left(v = \frac{h}{m\lambda}\right)$$

$$= \frac{1}{2} m \left(\frac{h}{m\lambda}\right)^2$$

$$= \frac{1}{2} \frac{h^2}{m\lambda^2}$$

or

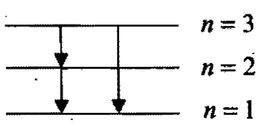
$$\lambda^2 = \frac{1}{2} \frac{h^2}{m \times \text{KE}}$$

$$\lambda = \frac{h}{\sqrt{2m \times \text{KE}}} \quad \begin{pmatrix} m = 9.108 \times 10^{-28} \text{ g} \\ h = 6.626 \times 10^{-27} \text{ erg -sec} \\ 1\text{eV} = 1.602 \times 10^{-12} \text{ erg} \end{pmatrix}$$

$$= \frac{6.626 \times 10^{-27}}{\sqrt{2 \times 9.108 \times 10^{-28} \times 2.5 \times 1.602 \times 10^{-12}}}$$

$$= 7.7 \times 10^{-8} \text{ cm}$$

Example 10. *Consider the following two electronic transition possibilities in a hydrogen atom as pictured below:*



(*a*) *The electron drops from third Bohr orbit to second Bohr orbit followed with the next transition from second to first Bohr orbit.*

(*b*) *The electron drops from third Bohr orbit to first Bohr orbit directly. Show that the sum of energies for the transitions* $n = 3$ *to* $n = 2$ *and* $n = 2$ *to* $n = 1$ *is equal to the energy of transition for* $n = 3$ *to* $n = 1$.

Solution: Applying, $\Delta E = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

For $n = 3$ to $n = 2$;

$$\Delta E_{3 \to 2} = R_H \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = R_H \times \frac{5}{36} \qquad \ldots \text{(i)}$$

For $n = 2$ to $n = 1$;

$$\Delta E_{2 \to 1} = R_H \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = R_H \times \frac{3}{4} \qquad \ldots \text{(ii)}$$

For $n = 3$ to $n = 1$;

$$\Delta E_{3 \to 1} = R_H \left[\frac{1}{1^2} - \frac{1}{3^2}\right] = R_H \times \frac{8}{9} \qquad \ldots \text{(iii)}$$

Adding equations (i) and (ii),

$$R_H \left(\frac{5}{36} + \frac{3}{4}\right) = R_H \left(\frac{5+27}{36}\right) = R_H \times \frac{8}{9}$$

Thus, $\Delta E_{3 \to 1} = \Delta E_{3 \to 2} + \Delta E_{2 \to 1}$

Example 11. *If an electron is moving with velocity* $500\, ms^{-1}$, *which is accurate up to 0.005% then calculate uncertainty in its position.* [$h = 6.63 \times 10^{-34}$ *Js, mass of electron* $= 9.1 \times 10^{-31}$ *kg*] **[AIPMT (Mains) 2008]**

Solution : Uncertainty in velocity

$$\Delta v = \frac{600 \times 0.005}{100} = 3 \times 10^{-2} \text{ ms}^{-1}$$

According to Heisenberg's uncertainty principle

$$\Delta x \, \Delta v \geq \frac{h}{4\pi m}$$

$$\Delta x \geq \frac{h}{4\pi m \Delta v}$$

$$\geq \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 3 \times 10^{-2}}$$

$$= 1.9 \times 10^{-3} \text{ m}$$

Example 12. *Applying Bohr's model when H atom comes from* $n = 4$ *to* $n = 2$, *calculate its wavelength. In this process, write whether energy is released or absorbed? Also write the range of radiation.* $R_H = 2.18 \times 10^{-18}$ *J*, $h = 6.63 \times 10^{-34}$ *Js*. **(AIPMT 2008)**

Solution : Energy is released in this process; and the radiation will belong to visible region (Balmer series)

$$E = \frac{hc}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = \frac{R_H Z^2}{hc} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= \frac{2.18 \times 10^{-18} \times 1^2}{6.63 \times 10^{-34} \times 3 \times 10^8} \left[\frac{1}{4} - \frac{1}{16}\right]$$

$$= \frac{2.18 \times 10^{-18} \times 1^2}{6.63 \times 10^{-34} \times 3 \times 10^8} \left[\frac{3}{16}\right]$$

$$\lambda = \frac{6.63 \times 10^{-34} \times 3 \times 10^8 \times 16}{3 \times 2.18 \times 10^{-18}} = 4866 \times 10^{-10} \text{ m}$$

$$= 4866 \text{ Å}$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Atom is the smallest indivisible particle of matter (proposed by John Dalton in 1808).

2. All atoms except hydrogen atom are composed of three fundamental particles, namely, electron, proton and neutron. Hydrogen atom has one electron and one proton but no neutron.

(a) Electron: The nature and existence of electron was established by experiments on conduction of electricity through gases, *i.e.*, discovery of cathode rays. In 1897, **J.J. Thomson** determined e/m value (-1.7588×10^8 coulomb/g) and proved that whatever gas be taken in the discharge tube and whatever be the material of the electrodes, the value of e/m is always the same. Electrons are, thus, common universal constituents of all atoms.

Electron is a subatomic particle which carries charge -1.60×10^{-19} coulomb, *i.e.*, one unit negative charge and has mass 9.1×10^{-28} g (or 9.1×10^{-31} kg), *i.e.*, $\frac{1}{1837}$th mass of hydrogen atom (0.000549 amu). The name electron was given by **Stoney.**

(b) Proton: The nature and existence of proton was established by the discovery of positive rays (**Goldstein** 1886). Proton is a subatomic particle which carries $+1.6 \times 10^{-19}$ coulomb or one unit positive charge and has mass 1.672×10^{-24} g (or 1.672×10^{-27} kg), *i.e.*, 1.0072 amu. The e/m was determined by **Thomson** in 1906 and the value is $+9.579 \times 10^4$ coulomb/g. It was named as proton by **Rutherford.**

(c) Neutron: It is a subatomic particle which carries no charge. Its mass is 1.675×10^{-24} g (1.675×10^{-27} kg) or 1.0086 amu. It is slightly heavier than proton. It was discovered by **Chadwick** in 1932 by bombarding beryllium with α-particles.

$$^{9}_{4}\text{Be} + ^{4}_{2}\text{He} \rightarrow ^{12}_{6}\text{C} + ^{1}_{0}n$$

The e/m value of neutron is zero.

3. According to the Rutherford's model of atom, (i) it consists of **nucleus** of very small size and high density (ii) electrons revolve round the nucleus in a circular path.

$$\text{Radius of nucleus} = 10^{-15} \text{ m}$$

$$\text{Density of nucleus} = 10^{8} \text{ tonnes/cc}$$

4. Atomic number (Z) = Number of protons in the nucleus

5. Mass number (A) = Number of protons + Number of neutrons

6. **Isotopes:** These are atoms of same element having same atomic number but different mass numbers, *e.g.*,

$$(^{1}_{1}\text{H}, ^{2}_{1}\text{H}, ^{3}_{1}\text{H}) : (^{35}_{17}\text{Cl}, ^{37}_{17}\text{Cl})$$

7. **Isobars:** These are atoms of different elements having same mass number but different atomic numbers, *e.g.*,

$$^{40}_{18}\text{Ar}, ^{40}_{19}\text{K}, ^{40}_{20}\text{Ca}$$

8. **Isotones:** These are atoms of different elements having same number of neutrons in the nucleus, *e.g.*,

$$^{14}_{6}\text{C}: ^{15}_{7}\text{N}, ^{16}_{8}\text{O}$$

9. Electromagnetic radiations are energy waves containing both electric and magnetic vector perpendicular to each other.

(i) These are transverse waves.

(ii) They do not need any medium for their propagation. They travel with the velocity of light.

(iii) $\nu = \frac{c}{\lambda}$, ν = frequency, c = velocity of light,

λ = wavelength

$\bar{\nu} = \frac{1}{\lambda}$ = wave number, $T = \frac{1}{\nu}$ = time period.

(iv) According to Planck's quantum theory, the energy is emitted or absorbed in the form of energy packets called **quanta. Quantum** of visible light is called **photon.**

Energy of one quantum $= h\nu$

$$= h\frac{c}{\lambda}$$

$$h = \text{Planck's constant}$$

$$= 6.626 \times 10^{-34} \text{ J sec}$$

10. **Hydrogen spectrum:** Hydrogen spectrum is a line spectrum. The lines lie in visible, ultraviolet and infrared regions. All the lines can be classified into five series. Ritz presented a mathematical formula to find the wavelengths of various lines,

$$\frac{1}{\lambda} = \bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where, R is Rydberg constant ($R = 109678 \text{ cm}^{-1}$).

		n_1	n_2
Lyman series	(UV region)	1	2, 3, 4, 5, ...
Balmer series	(Visible region)	2	3, 4, 5, 6, ...
Paschen series	(IR region)	3	4, 5, 6, 7, ...
Brackett series	(IR region)	4	5, 6, 7, 8, ...
Pfund series	(IR region)	5	6, 7, 8, 9, ...

Balmer series consists of four prominent lines H_α, H_β, H_γ and H_δ having wavelength 6563 Å, 4861 Å, 4340 Å and 4102 Å respectively.

Balmer equation is,

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

where, $n = 3, 4, 5, 6, \ldots$

The Rydberg formula is used to calculate the wavelength of any line of the spectrum

$$\frac{1}{\lambda}=RZ^2\left[\frac{1}{n_1^2}-\frac{1}{(n_1+x)^2}\right]$$

where, x = number of lines in the spectrum; $x=\infty$ for series limit or last line. Let, transition of electrons takes place from n_2 to n_1 shell; then the number of lines can be calculated as:

$$\text{Number of lines}=\frac{(n_2-n_1)(n_2-n_1+1)}{2}$$

11. Bohr's atomic model: It is based on Planck's quantum theory. Its main postulates are summarised as:

(i) Electrons revolve round the nucleus in circular path of fixed energy called **stationary states.**

(ii) Angular momentum of electrons are quantised, *i.e.*,

$$mvr=n\left(\frac{h}{2\pi}\right)$$

(iii) The energy as well as angular momentum both are quantised for electrons. It means they can have only certain values of energy and angular momenta.

12. Important formulations obtained from Bohr's atomic model which are valid for single electron species like H, He^+, Li^{2+}, Be^{3+}, etc.:

(i) $E_1<E_2<E_3<E_4$

(ii) $(E_2-E_1)>(E_3-E_2)>(E_4-E_3)\ldots$

where, $E_1,E_2,E_3,\ldots$ are energies of corresponding shells.

(iii) $$r_n=\frac{n^2h^2}{4\pi^2Ke^2mZ}$$

$$K=\frac{1}{4\pi\varepsilon_0}=9\times10^9\ \text{Nm}^2/\text{C}^2$$

$r=\dfrac{n^2}{Z}\times0.529$ Å (where, r is the radius of Bohr orbit of electrons.)

(iv) Energy of electrons in a particular shell can be calculated as:

$$E=-\frac{Z^2}{n^2}\frac{2\pi^2mK^2e^4}{h^2}$$

$$E=-\frac{Z^2}{n^2}\times21.79\times10^{-19}\ \text{J/atom}$$

$$=-\frac{Z^2}{n^2}\times13.6\text{eV}$$

$$=-\frac{Z^2}{n^2}\times1312\ \text{kJ/mol}$$

$$E_n=\frac{Z^2R_E}{n^2}$$

$R_E=-13.6$ eV (Rydberg energy)

(v) $E_n=E_1/n^2$; $E_n=E_1\times\dfrac{Z^2}{n^2}$ for hydrogen-like species.

(vi) Velocity of electrons in a particular shell or orbit can be calculated as:

$$v=\sqrt{\frac{Ke^2}{mr}}$$

where, $K=\dfrac{1}{4\pi\varepsilon_0}=9\times10^9\ \text{Nm}^2/\text{C}^2$

$$v=\frac{Z}{n}\times2.188\times10^8\ \text{cm/sec}$$

(vii) Potential energy of electrons in a particular shell:

$$\text{PE}=\frac{-KZe^2}{r}=-\frac{27.2}{n^2}\times Z^2\ \text{eV}$$

(viii) Kinetic energy of electrons in a particular shell:

$$\text{KE}=\frac{1}{2}\frac{KZe^2}{r}=+\frac{13.6}{n^2}Z^2\ \text{eV}$$

$$\text{Total Energy, TE}=-\frac{1}{2}\frac{KZe^2}{r}$$

$$\text{TE}=\frac{1}{2}\text{PE}$$

$$\text{TE}=-\text{KE}$$

(ix) Number of revolutions per second by an electron in a shell:

$$=\frac{\text{Velocity}}{\text{Circumference}}=\frac{v}{2\pi r}=-\frac{E_1}{h}\times\frac{2}{n^3}$$

(x) Frequency of electrons in nth orbit:

$$=\frac{v}{2\pi r}$$

$$=\frac{6.62\times10^{15}Z^2}{n^3}$$

(xi) Period of revolution of electrons in nth orbit (T_n),

$$T_n=\frac{2\pi r}{V_n}=\frac{1.5\times10^{-16}n^3}{Z^2}\ \text{sec}$$

$$T\propto\frac{n^3}{Z^2}$$

(xii) Ionization energy $=E_\infty-E_n$

$$=0-\left(-\frac{Z^2}{n^2}\times13.6\text{eV}\right)$$

$$=\frac{Z^2}{n^2}\times13.6\text{eV}$$

$$=\frac{Z^2}{n^2}\times21.79\times10^{-19}\ \text{J/atom}$$

(xiii) $$\frac{I_1}{I_2}=\frac{Z_1^2}{Z_2^2}\times\frac{n_2^2}{n_1^2}$$

I_1 and I_2 are ionization energies of two elements 1 and 2.

(xiv) ΔE (Energy of transition) $=R_E\left(\dfrac{1}{n_1^2}-\dfrac{1}{n_2^2}\right)$

$R_E=-13.6$ eV

R_H = Rydberg constant $= \frac{R_E}{hc} = 109677\ cm^{-1}$

Defects of Bohr theory: (i) It fails to explain the spectra of multi-electron atoms. (ii) It fails to explain fine spectrum of hydrogen. (iii) It does not provide an explanation why angular momentum should always be an integral multiple of $h/2\pi$. (iv) It does not explain splitting of spectral lines under the influence of magnetic field (Zeeman effect) and electric field (Stark effect).

13. Sommerfeld's extension: Sommerfeld (1915) introduced the idea of elliptical orbits. Except first orbit which is only circular, the other orbits are elliptical. The second orbit has one elliptical and one circular suborbit. The third orbit has two elliptical and one circular suborbit.

14. Dual nature: Light has dual character, *i.e.*, it behaves sometimes like particles and sometimes like waves. de Broglie (1924) predicted that small particles such as electrons should show wave-like properties along with particle character. The wavelength (λ) associated with a particle of mass m and moving with velocity v is given by the relationship $\lambda = \frac{h}{mv}$; where, h is Planck's constant.

The wave nature was confirmed by Davisson and Germer's experiment.

Davisson and Germer gave some modified equations for calculation of de Broglie wavelength:

$\lambda = \frac{h}{\sqrt{2Em}}$; where, E = kinetic energy of the particle.

$\lambda = \frac{h}{\sqrt{2qVm}}$; where, q = charge of the particle accelerated by the potential of V volt.

15. Heisenberg uncertainty principle: It is impossible to measure simultaneously both the position and momentum of any microscopic particle with accuracy. Mathematically, $\Delta x\, \Delta p \approx \frac{h}{4\pi}$; where, Δx = uncertainty in position and Δp = uncertainty in momentum. It introduces the concept of probability of locating the electron in space around the nucleus.

16. de Broglie concept as well as uncertainty principle have no significance in everyday life because they are significant for only microscopic systems.

17. When radiations of a certain minimum frequency (ν_0), called threshold frequency, strike the surface of a metal, electrons called photoelectrons are ejected from the surface. The minimum energy required to eject the electrons from the metal surface is called threshold energy or work function.

Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$E = E_0 + \text{KE}$$

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \frac{1}{2}mv^2$$

ν_0 and λ_0 are called threshold frequency and threshold wavelength respectively.

18. Quantum numbers: The set of four integers required to define an electron completely in an atom are called quantum numbers. The first three have been derived from Schrödinger's wave equation.

(i) Principal quantum number: It describes the name, size and energy of the shell to which the electron belongs.

$n = 1, 2, 3, 4, \ldots$ represent K, L, M, N, ... shells respectively.

Formulae for radius, energy and angular momentum of electrons are given earlier.

(ii) Azimuthal quantum number: It is denoted by 'l'. It describes the shape of electron cloud and number of subshells in a shell.

$$l = 0, 1, 2, 3, \ldots, (n-1)$$

$l = 0$ (s-subshell); $l = 1$ (p-subshell); $l = 2$ (d-subshell); $l = 3$ (f-subshell).

Orbital angular momentum of electron

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{l(l+1)}\,\hbar$$

when $l = 0$, electrons revolve in a circular orbit and when $l \neq 0$, the electrons revolve round the nucleus in an elliptical path.

(iii) Magnetic quantum number: It is denoted by 'm'. It describes the orientations of the subshells. It can have values from $-l$ to $+l$ including zero, *i.e.*, total $(2l+1)$ values. Each value corresponds to an orbital. s-subshell has one orbital, p-subshell has three orbitals (p_x, p_y and p_z), d-subshell has five orbitals (d_{xy}, d_{yz}, $d_{zx}, d_{x^2-y^2}$ and d_{z^2}) and f-subshell has seven orbitals. One orbital can accommodate either one or two electrons but not more than two. s-orbital is spherically symmetrical and non-directional. p-orbitals have dumb-bell shape and are directional in nature. Four d-orbitals have double dumb-bell shape but d_{z^2} has a baby soother shape. The total number of orbitals present in a main energy level is 'n^2'.

(iv) Spin quantum number (s): It describes the spin of the electron. It has values +1/2 and −1/2. (+) signifies clockwise spinning and (−) signifies anticlockwise spinning.

$$\text{Spin angular momentum} = \sqrt{s(s+1)}\,\frac{h}{2\pi}$$

$$= \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar \quad \left(\text{where, } s = \frac{1}{2}\right)$$

Total spin of an atom or an ion $= n \times \frac{1}{2}$; where, 'n' is the number of unpaired electrons.

Spin multiplicity of an atom $= (2\Sigma s + 1)$

Singlet state (Normal)

$\uparrow\downarrow$

Spin multiplicity

$= 2\Sigma s + 1$

$= 2 \times 0 + 1 = 1$

Singlet excited

$\downarrow$

$\uparrow$

Spin multiplicity = 1

Triplet excited state

$\uparrow$

$\uparrow$

Spin multiplicity

$= 2 \times \left(\frac{1}{2} + \frac{1}{2}\right) + 1 = 3$

19. (i) Number of subshells in a shell = n

(ii) Number of maximum orbitals in a shell = n^2

(iii) Number of maximum orbitals in a subshell = $2l + 1$

(iv) Maximum number of electrons in a shell = $2n^2$

(v) Maximum number of electrons in a subshell $= 2(2l + 1)$

(vi) Z-component of the angular momentum depends upon magnetic quantum number and is given as:

$$L_Z = m\left(\frac{h}{2\pi}\right)$$

(vii) Number of radial/spherical nodes in any orbital $= (n - l - 1)$

1s orbital has no node; 2s orbital has one spherical node; $2p$ orbital has no spherical node; $3p$ orbital has one spherical node.

(viii) Schrödinger wave equation does not give spin quantum number.

(ix) A plane passing through the nucleus at which the probability of finding the electron is zero, is called nodal plane.

The number of nodal plane in an orbital = l

s-orbitals have no nodal plane; p-orbitals have one nodal plane, d-orbitals have two nodal planes and so on.

20. Pauli's exclusion principle: No two electrons in an atom can have the same set of all the four quantum numbers, *i.e.*, an orbital cannot have more than 2 electrons because three quantum numbers (principal, azimuthal and magnetic) at the most may be same but the fourth must be different, *i.e.*, spins must be in opposite directions. It is possible to calculate the maximum number of electrons which can be accommodated on a main energy shell or subenergy shell on the basis of this principle.

21. Electronic configuration: The arrangement of electrons in various shells, subshells and orbitals in an atom is termed electronic configuration. It is written in terms of nl^x where n indicates the order of shell, l indicates the subshell and x the number of electrons present in the subshell.

22. Aufbau principle: Aufbau is a German word meaning building up. The electrons are filled in various orbitals in an order of their increasing energies. An orbital of lowest energy is filled first. The sequence of orbitals in the order of their increasing energy is:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, ...

The energy of the orbitals is governed by $(n + l)$ rule.

(i) Subshell with lower of $(n + l)$ has lower energy, hence filled first, *e.g.*,

$3p(n + l = 4)$ will be filled before $3d(n + l = 5)$.

(ii) When $(n + l)$ values are same, then the subshell with lower value of 'n' is filled first, *e.g.*,

$3p(n + l = 4)$ will be filled before $4s(n + l = 4)$ because $3p$ has lower value of n.

23. Hund's rule: No electron pairing takes place in the orbitals in a subenergy shell until each orbital is occupied by one electron with parallel spin. Exactly half-filled and fully-filled orbitals make the atoms more stable, *i.e.*, $p^3, p^6, d^5, d^{10}, f^7$ and f^{14} configurations are most stable.

All those atoms which consist of at least one orbital singly occupied behave as **paramagnetic** while all those atoms in which all the orbitals are doubly occupied are **diamagnetic** in nature.

Magnetic moment $= \sqrt{n(n + 2)}$ BM

n = number of unpaired electrons

24. Half-filled and fully-filled subshells have extra stability due to **greater exchange energy** and **spherical symmetry** around the nucleus.

25. It is only dz^2 orbitals which do not have four lobes like other d-orbitals.

26. The d-orbital whose lobes lie along the axes is $d_{x^2-y^2}$.

27. Wave mechanical model of atom: It was Schrödinger who developed a new model known as wave mechanical model of atom by incorporating the conclusions of de Broglie and Heisenberg uncertainty principles. He derived an equation, known as Schrödinger equation.

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

The solution of the equation provides data which enables us to calculate the probability of finding an electron of specific energy. It is possible to determine the regions of space around the nucleus where there is maximum probability of locating an electron of specific energy. This region of space is termed orbital.

ψ is the amplitude of the wave at a point with coordinates x, y and z. 'E' is total energy called eigen value and V denotes the potential energy of the electron.

ψ^2 gives the probability of finding the electron at (x, y and z).

Operator form of the equation can be given as:

$$\hat{H}\psi = E\psi$$

$$\hat{H} = \left[-\frac{h^2}{8\pi^2 m} \Delta^2 + \hat{V} \right] \text{called Hamiltonian operator}$$

$$= \hat{T} + \hat{V}$$

$\hat{T}$ = Kinetic energy operator

$\hat{V}$ = Potential energy operator

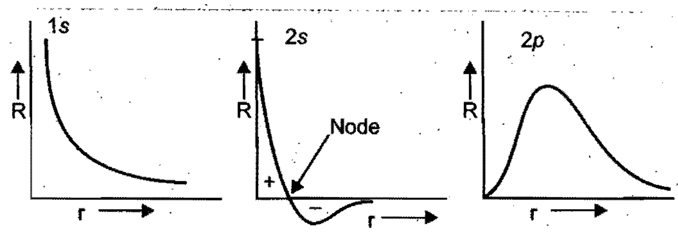
28. Complete wave function can be given as:

$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{Radial part}} \; ; \underbrace{\Theta(\theta)\,\Phi(\phi)}_{\text{Angular part}}$$

Dependence of the wave function on quantum number can be given as:

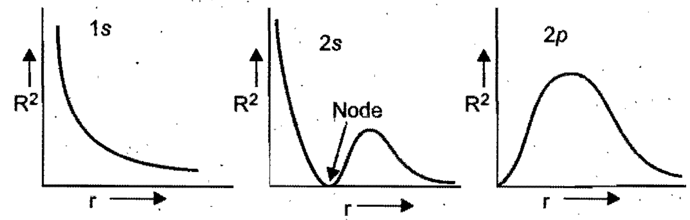
$$\psi_{nlm}(r,\theta,\phi) = R_{n,l}(r)\,\Theta_{lm}(\theta)\,\Phi_m(\phi)$$

29. Graph of radial wave function 'R': At node, the value of 'R' changes from positive to negative.

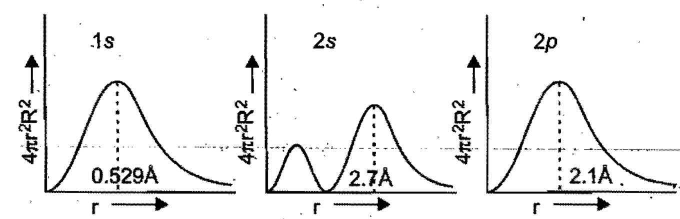


Number of radial nodes = $(n - l - 1)$.

30. Plot of radial probability density 'R^2':



31. Plot of radial probability function ($4\pi r^2 R^2$):



In the plot of radial probability against 'r', number peaks, *i.e.*, region of maximum probability = $n - l$.

Questions

1. Match the following:

[A]

(i) Aufbau principle	(a) Line spectrum in visible region
(ii) de Broglie	(b) Orientation of an electron in an orbital
(iii) Angular momentum	(c) Photon
(iv) Hund's rule	(d) $\lambda = h/(mv)$
(v) Balmer series	(e) Electronic configuration
(vi) Planck's law	(f) mvr

[B]

(i) Thomson	(a) Exclusion principle
(ii) Pauli	(b) Radioactivity
(iii) Becquerel	(c) Atomic model
(iv) Soddy	(d) Cathode rays
(v) Bohr	(e) Neutron
(vi) Chadwick	(f) Isotopes

[C]

(i) Cathode rays	(a) Helium nuclei
(ii) Dumb-bell	(b) Uncertainty principle
(iii) Alpha particles	(c) Electromagnetic radiation
(iv) Moseley	(d) p-orbital
(v) Heisenberg	(e) Atomic number
(vi) X-rays	(f) Electrons

2. **Matrix Matching Problems (For IIT Aspirants):**

[A] Match the Column-I and Column-II:

Column-I	Column-II
(a) X-rays	(p) Davisson and Germer experiment
(b) Atomic number determination	(q) Crystal structure determination
(c) Dual nature of matter	(r) Moseley's law
(d) Dual nature of radiation	(s) Bragg's law

[B] Match the Column-I and Column-II:

Column-I	Column-II
(a) Lyman series	(p) Visible region
(b) Balmer series	(q) UV region
(c) Pfund series	(r) IR region
(d) Light emitted by sodium lamp	(s) Line emission spectrum

[C] Match the List-I with List-II in hydrogen atom spectrum:

List-I	List-II
(a) Lyman series	(p) Visible region
(b) Balmer series	(q) Infrared region
(c) Paschen series	(r) Absorption spectrum
(d) Brackett series	(s) Ultraviolet region

[D] Match the List-I with List-II:

List-I	List-II
(a) K-shell	(p) Electrons in elliptical orbit
(b) L-shell	(q) Electrons in circular orbit
(c) Hydrogen atom	(r) Shell of lowest energy
(d) Boron atom in ground state	(s) Bohr's atomic model

[E] Match the ions of List-I with the properties of List-II:

List-I	List-II
(a) Mn^{2+}	(p) Diamagnetic
(b) V^{2+}	(q) Paramagnetic
(c) Zn^{2+}	(r) Coloured compounds
(d) Ti^{4+}	(s) Magnetic moment = 2.82 BM

[F] Match the List-I with List-II:

List-I	List-II
(a) Mg^{2+}	(p) Zero spin multiplicity
(b) Fe^{2+}	(q) Spin multiplicity = 3
(c) Co^{3+}	(r) Total spin = 0
(d) Ca^{2+}	(s) Total spin = 2

[G] Match the properties of List-I with the formulae in List-II:

List-I	List-II
(a) Angular momentum of electron	(p) $\sqrt{l(l+1)}\frac{h}{2\pi}$
(b) Orbital angular momentum	(q) $I\omega$
(c) Wavelength of matter wave	(r) $nh/2\pi$
(d) Quantised value(s)	(s) h/p

[H] Match the orbitals of List-I with the nodal properties of List-II:

List-I	List-II
(a) $2s$	(p) Angular node = 1
(b) $1s$	(q) Radial node = 0
(c) $2p$	(r) Radial node = 1
(d) $3p$	(s) Angular node = 0

[I] Match the electronic transitions of List-I with spectral properties of List-II:

List-I	List-II
(a) $n = 6 \longrightarrow n = 3$	(p) 10 lines in the spectrum
(b) $n = 7 \longrightarrow n = 3$	(q) Spectral lines in visible region
(c) $n = 5 \longrightarrow n = 2$	(r) 6 lines in the spectrum
(d) $n = 6 \longrightarrow n = 2$	(s) Spectral lines in infrared region

[J] Match the List-I with List-II:

List-I	List-II
(a) Radius of electron orbit	(p) Principal quantum number
(b) Energy of electron	(q) Azimuthal quantum number
(c) Energy of subshell	(r) Magnetic quantum number
(d) Orientation of the atomic orbitals	(s) Spin quantum number

[K] Match the List-I with List-II:

List-I	List-II
(a) Electron cannot exist in the nucleus	(p) de Broglie wave
(b) Microscopic particles in motion are associated with	(q) Electromagnetic wave
(c) No medium is required for propagation	(r) Uncertainty principle
(d) Concept of orbit was replaced by orbital	(s) Transverse wave

[L] According to Bohr theory: **(IIT 2006)**

E_n = Total energy
K_n = Kinetic energy
V_n = Potential energy
r_n = Radius of nth orbit

Match the following:

Column-I	Column-II
(a) $V_n / K_n = ?$	(p) 0
(b) If radius of nth orbit $\propto En^x$; $x = ?$	(q) -1
(c) Angular momentum in lowest orbital	(r) -2
(d) $\frac{1}{r^n} \propto Z^y$; $y = ?$	(s) 1

[M] Match the List-I with List-II:

List-I	List-II
(a) Radius of nth orbital	(p) Inversely proportional to Z
(b) Energy of nth shell	(q) Integral multiple of $h/2\pi$
(c) Angular momentum of electron	(r) Proportional to n^2
(d) Velocity of electron in nth orbit	(s) Inversely proportional to 'n'

[N] Match the entries in Column-I with the correctly related quantum number(s) in Column-II:

Column-I	Column-II
(a) Orbital angular momentum of the electron in a hydrogen-like atomic orbital	(p) Principal quantum number
(b) A hydrogen-like one electron wave function obeying Pauli principle	(q) Azimuthal quantum number
(c) Shape, size and orientation of hydrogen-like atomic orbitals	(r) Magnetic quantum number
(d) Probability density of electron at the nucleus in hydrogen-like atom	(s) Electron spin quantum number

[O] Match the List-I with List-II: **(IIT 2006)**

List-I	List-II
(a) Wave nature of radiation	(p) Photoelectric effect
(b) Photon nature of radiation	(q) Compton effect
(c) Interaction of a photon with an electron, such that quantum energy is slightly equal to or greater than the binding energy of electron, is more likely to result in:	(r) Diffraction
(d) Interaction of a photon with an electron, such that photon energy is much greater than the binding energy of electron, is more likely to result in:	(s) Interference

[P] Match the Column-I with Column-II:

Column-I	Column-II
(a) Orbital angular momentum of an electron	(p) $\sqrt{s(s+1)}\,h/2\pi$
(b) Angular momentum of electron	(q) $\sqrt{n(n+2)}$ BM
(c) Spin angular momentum of electron	(r) $nh/2\pi$
(d) Magnetic moment of atom	(s) $\sqrt{l(l+1)}\,h/2\pi$

[Q] Match the Column-I with Column-II:

Column-I	Column-II
(a) Scintillation	(p) Wave nature
(b) Photoelectric effect	(q) Particle nature
(c) Diffraction	(r) Particle nature dominates over wave nature
(d) Principle of electron microscope	(s) Wave nature dominates over particle nature

[R] Match the Column-I with Column-II:

Column-I	Column-II
(a) Radial function R	(p) Principal quantum number 'n'
(b) Angular function Θ	(q) Azimuthal quantum number 'l'
(c) Angular function Φ	(r) Magnetic quantum number 'm'
(d) Quantized angular momentum	(s) Spin quantum number 's'

Answers

1. [A] (i—e); (ii—d); (iii—f); (iv—b); (v—a); (vi—c)
   [B] (i—d); (ii—a); (iii—b); (iv—f); (v—c); (vi—e)
   [C] (i—f); (ii—d); (iii—a); (iv—e); (v—b); (vi—c)
2. [A] (a—q, r, s) (b—r) (c—p) (d—does not match)
   [B] (a—q, s) (b—p, s) (c—r, s) (d—p, s)
   [C] (a—r, s) (b—p) (c—q) (d—q)
   [D] (a—q, r) (b—p, q) (c—s) (d—p, q)
   [E] (a—q, r) (b—q, r, s) (c—p) (d—p)
   [F] (a—p, r) (b—q, s) (c—q, s) (d—p, r)
   [G] (a—q, r) (b—p) (c—s) (d—q, r)
   [H] (a—r, s) (b—q, s) (c—q, p) (d—p, r)
   [I] (a—r, s) (b—p, s) (c—q, r) (d—p, q)
   [J] (a—p) (b—p) (c—p, r) (d—r)
   [K] (a—r) (b—p) (c—q, s) (d—r)
   [L] (a—r) (b—q) (c—p) (d—s)
   [M] (a—r, p) (b—r) (c—q) (d—s)
   [N] (a—p) (b—s) (c—p, q, r) (d—p, q)
   [O] (a—r, s) (b—p, q) (c—p) (d—q)
   [P] (a—s) (b—r) (c—p) (d—q)
   [Q] (a—q) (b—r) (c—p) (d—p, s)
   [R] (a—p, q) (b—q, r) (c—r) (d—q, s)

• PRACTICE PROBLEMS •

1. An atom of an element contains 13 electrons. Its nucleus has 14 neutrons. Find out its atomic number and approximate atomic mass. An isotope has atomic mass 2 units higher. What will be the number of protons, neutrons and electrons in the isotope?
   [Ans. At. No. = 13, atomic mass = 27; the isotope will have same number of protons and electrons = 13 but neutrons will be 14 + 2 = 16]
2. From the following find out groups of isotopes, isobars and isotones:
   $$^{16}_{8}O,\ ^{39}_{19}K,\ ^{14}_{6}C,\ ^{239}_{92}U,\ ^{14}_{7}N,\ ^{40}_{20}Ca,\ ^{238}_{92}U,\ ^{77}_{32}Ge,$$
   $$^{77}_{33}As,\ ^{18}_{8}O,\ ^{76}_{32}Ge,\ ^{78}_{34}Se$$
   [Ans. Isotopes—same at. no. but different at. masses.
   $$^{16}_{8}O,\ ^{18}_{8}O;\ ^{239}_{92}U,\ ^{238}_{92}U;\ ^{77}_{32}Ge,\ ^{76}_{32}Ge$$
   Isobars—same atomic masses but different at. numbers
   $$^{14}_{6}C,\ ^{14}_{7}N;\ ^{77}_{32}Ge,\ ^{77}_{33}As$$
   Isotones—same number of neutrons.
   $$^{16}_{8}O,\ ^{14}_{6}C;\ ^{39}_{19}K,\ ^{40}_{20}Ca;\ ^{77}_{33}As,\ ^{78}_{34}Se]$$
3. An element has atomic number 30. Its cation has 2 units positive charge. How many protons and electrons are present in the cation?
   [Ans. Protons = 30, Electrons = 28]
4. Calculate the number of neutrons in 18 mL of water. (Density of water = 1)
   [Ans. 48.16×10^{23}]
   [Hint: One molecule of water contains = 8 neutrons]
5. Find (i) the total number of neutrons and (ii) the total mass of neutrons in 7 mg of ^{14}C (assuming that mass of neutron = mass of hydrogen atom).
   [Ans. (i) 24.08×10^{20} and (ii) 4 mg]
6. Calculate the wavelength of a photon in Angstroms having an energy of 1 electron volt.
   [Hint: $1\ eV = 1.602 \times 10^{-19}$ joule;
   $$h = 6.62 \times 10^{-34}\ J\text{-}s,\ c = 3 \times 10^{8}\ ms^{-1}$$
   $$\lambda = \frac{h \cdot c}{E} = 12.42 \times 10^{-7}\ m = 12.42 \times 10^{3}\ Å]$$
7. A photon of light with wavelength 6000 Å has an energy E. Calculate the wavelength of photon of a light which corresponds to an energy equal to $2E$.
   [Ans. 3000 Å]
8. Calculate the energy in kilocalorie per mol of the photons of an electromagnetic radiation of wavelength 5700 Å.
   [Ans. 56.3 kcal per mol]

9. Light of what frequency and wavelength is needed to ionise sodium atom. The ionisation potential of sodium is 8.2×10^{-19} J.

[**Ans.** $\nu = 1.238 \times 10^{15}$ Hz; $\lambda = 242$ nm]

10. Determine the energy of 1 mole photons of radiations whose frequency is $5 \times 10^{10}\ s^{-1}$. ($h = 6.62 \times 10^{-34}$ J-s)

[**Ans.** 19.9 J]

11. Find e/m for He^{2+} ion and compare with that for electron.
[**Ans.** 4.87×10^7 coulomb kg^{-1}]

12. A ball of mass 100 g is moving with a velocity of 100 m sec^{-1}. Find its wavelength.

[**Hint:** $\lambda = \dfrac{h}{mv} = \dfrac{6.626 \times 10^{-34}}{0.1 \times 100} = 6.626 \times 10^{-35}$ m]

13. Calculate the wavelength of radiation and energy per mol necessary to ionize a hydrogen atom in the ground state.
[**Ans.** $\lambda = 9.12 \times 10^{-8}$ m; 1313 kJ / mol]

14. Bond energy of F_2 is 150 kJ mol^{-1}. Calculate the minimum frequency of photon to break this bond.
[**Ans.** $3.759 \times 10^{14}\ s^{-1}$]

15. If an Einstein (E) is the total energy absorbed by 1 mole of a substance and each molecule absorbs one quantum of energy, then calculate the value of 'E' in terms of λ in cm.

[**Ans.** $\dfrac{1.198 \times 10^8}{\lambda}$ erg mol^{-1}]

16. How many chlorine atoms can you ionize in the process? $Cl \rightarrow Cl^+ + e$ by the energy liberated from the following process:

$$Cl + e \rightarrow Cl^- \text{ for } 6 \times 10^{23} \text{ atoms}$$

given that electron affinity of chlorine is 3.61 eV and ionization energy of chlorine is 17.422 eV.

[**Ans.** 1.24×10^{23} atoms]

17. Find the velocity (ms^{-1}) of electron in first Bohr orbit of radius a_0. Also find the de Broglie wavelength (in 'm'). Find the orbital angular momentum of $2p$ orbital of hydrogen atom in units of $h/2\pi$.

[**Hint:** $v = \dfrac{2.188 \times 10^6}{n}$ m sec^{-1}

$$v = \frac{2.188 \times 10^6}{1} = 2.188 \times 10^6 \text{ m sec}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.188 \times 10^6}$$

$$= 3.3 \times 10^{-10} \text{ m}$$

$$\text{Orbital angular momentum} = \sqrt{l(l+1)}\,\frac{h}{2\pi}$$

$$= \sqrt{1(1+1)}\,\frac{h}{2\pi} \qquad (\because l = 1 \text{ for } 2p)$$

$$= \sqrt{2}\,\frac{h}{2\pi}\ ]$$

18. The energy of an α-particle is 6.8×10^{-18} J. What will be the wavelength associated with it? **[CBSE-PMT (Mains) 2005]**

[**Hint:** $\lambda = \dfrac{h}{\sqrt{2Em}} = \dfrac{6.626 \times 10^{-34}}{\sqrt{2 \times 6.8 \times 10^{-18} \times 4 \times 1.66 \times 10^{-27}}}$

$= 2.2 \times 10^{-12}$ m]

19. Determine the number of revolutions made by an electron in one second in the 2nd Bohr orbit of H-atom.

[**Ans.** $n = \dfrac{2\pi r}{v}$]

20. What is the speed of an electron whose de Broglie wavelength is 0.1 nm? By what potential difference, must have such an electron accelerated from an initial speed zero?
[**Ans.** 7.28×10^6 m/sec; 150 V]

21. A green ball weighs 75 g; it is travelling towards observer at a speed of 400 cm/sec. The ball emits light of wavelength 5×10^{-5} cm. Assuming that the error in the position of ball is the same as wavelength of itself, calculate error in the momentum of the green ball.

[**Hint:** $\Delta x \cdot \Delta p \geq \dfrac{h}{4\pi}$

$$\Delta p \geq \frac{h}{4\pi\,\Delta x}$$

$$\Delta p \geq \frac{h}{4\pi\lambda}$$

$$\Delta p \approx \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 5 \times 10^{-5}} \approx 1.055 \times 10^{-23}\ ]$$

22. What is the relationship between the eV and the wavelength in metre of the energetically equivalent photons?
[**Ans.** $\lambda = 12.4237 \times 10^{-7}$ metre]

23. What is the velocity of an electron ($m = 9.11 \times 10^{-31}$ kg) in the innermost orbit of the hydrogen atom?
(Bohr radius $= 0.529 \times 10^{-10}$ m)

[**Ans.** 2.187×10^6 m/sec]

24. In a hydrogen atom, an electron jumps from the third orbit to the first orbit. Find out the frequency and wavelength of the spectral line. ($R_H = 1.09678 \times 10^7\ m^{-1}$)

[**Ans.** 2.925×10^{15} Hz, 1025.6 Å]

25. The energy of the electron in the second and third Bohr orbits of hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.
[**Ans.** 6.6×10^3 Å]

26. Calculate the wavelength in angstroms of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionisation potential of the ground state of hydrogen atom is 2.17×10^{-11} erg per atom.

[**Hint:** Energy of the electron in the 1st orbit = – (ionisation potential), $\Delta E = (3/4) \times 2.17 \times 10^{-11}$ erg per atom]

[**Ans.** $\lambda = 1220$ Å]

27. Calculate the wave number for the shortest wavelength transition in Balmer series of atomic hydrogen. **(IIT 1996)**
[**Ans.** 27419.25 cm^{-1}]

28. The wavelength of the first member of the Balmer series of hydrogen is 6563×10^{-10} m. Calculate the wavelength of its second member.

[Hint: $\frac{1}{\lambda_1} = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$ and $\frac{1}{\lambda_2} = R_H\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$

$$\frac{\lambda_2}{\lambda_1} = \frac{5}{36} \times \frac{16}{3} = \frac{20}{27}$$

$$\lambda_2 = \frac{20}{27} \times 6563 \times 10^{-10} = 4861 \times 10^{-10} \text{ m}]$$

29. According to Bohr theory, the electronic energy of hydrogen atom in the nth Bohr orbit is given by,

$$E_n = -\frac{21.76 \times 10^{-19}}{n^2} \text{ J}$$

Calculate the longest wavelength of light that will be needed to remove an electron from the 2nd orbit of Li^{2+} ion.

[Ans. 4.059×10^{-8} m]

30. Calculate the frequency, energy and wavelength of the radiation corresponding to spectral line of lowest frequency in Lyman series in the spectra of hydrogen atom. Also calculate the energy of the corresponding line in the spectra of Li^{2+}.

(IIT 1991)

[Ans. $\lambda = 1.216 \times 10^{-7}$ m, $v = 2.47 \times 10^{15}$ cycle sec^{-1}, $E = 16.36 \times 10^{-19}$ J, $E_{Li^{2+}} = Z^2 \times E_H = 9 \times 16.36 \times 10^{-19}$ J $= 147.27 \times 10^{-19}$ J]

31. Calculate the ratio of the velocity of light and the velocity of electron in the 2nd orbit of a hydrogen atom. (Given $h = 6.624 \times 10^{-27}$ erg-sec; $m = 9.108 \times 10^{-28}$ g; $r = 2.11 \times 10^{-8}$ cm)

[Ans. 273.2]

32. What hydrogen-like ion has the wavelength difference between the first lines of Balmer and Lyman series equal to 59.3 nm ($R_H = 109678$ cm^{-1})?

[Hint: Wavelength of 1st line in Balmer series,

$$\frac{1}{\lambda_B} = Z^2 R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5}{36} R_H Z^2$$

or $$\lambda_B = \frac{36}{5R_H Z^2}$$

Wavelength of 1st line in Lyman series is,

$$\frac{1}{\lambda_L} = Z^2 R_B\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

or $$\lambda_L = \frac{4}{3 \times R_H Z^2}$$

$$\text{Difference } \lambda_B - \lambda_L = 59.3 \times 10^{-7} = \frac{36}{5R_H Z^2} - \frac{4}{3R_H Z^2}$$

$$= \frac{1}{R_H Z^2}\left[\frac{36}{5} - \frac{4}{3}\right]$$

$$Z^2 = \frac{88}{59.3 \times 10^{-7} \times 109678 \times 15} = 9.0$$

or $$Z = 3$$

Hydrogen-like species is Li^{2+}.]

33. The velocity of an electron in certain Bohr orbit of H-atom bears the ratio 1 : 275 to the velocity of light. (a) What is the quantum number 'n' of the orbit? (b) Calculate the wave number of the radiation when the electron jumps from $(n + 1)$ state to ground state.

[Ans. $\bar{v} = 9.75 \times 10^4$ cm^{-1}]

[Hint: (a) $\frac{v}{c} = \frac{1}{275}$ or $v = \frac{3 \times 10^{10}}{275} = 1.09 \times 10^8$ cm sec^{-1}

$$v = \frac{nh}{2\pi mr} = \frac{nh}{2\pi m \times 0.529 \times 10^{-8} \times n^2}$$

or $$n = \frac{h}{2\pi m \times 0.529 \times 10^{-8} \times v}$$

$$= \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 9.1 \times 10^{-28} \times 0.529 \times 10^{-8} \times 1.09 \times 10^8}$$

$$= 2$$

(b) Thus, $n + 1 = 2 + 1 = 3$. The electron jumps from 3rd orbit to 1st orbit.]

34. Find out the wavelength of the next line in the series having lines of spectrum of H-atom of wavelengths 6565 Å, 4863 Å, 4342 Å and 4103 Å.

[Ans. 3972 Å]

[Hint: All these lines are in visible region and thus, belong to Balmer series. Next line is, therefore, from 7th orbit.]

35. Which jump is responsible for the wave number of emitted radiations equal to 9.7490×10^6 m^{-1} in Lyman series of hydrogen spectrum? ($R = 1.09678 \times 10^7$ m^{-1})

[Ans. 3]

36. Calculate the ionisation energy of the hydrogen atom. How much energy will be required to ionise 1 mole of hydrogen atoms? Given, that the Rydberg constant is 1.0974×10^7 m^{-1}.

[Ans. IE per hydrogen atom = 2.182×10^{-18} J
IE per mole = 1314 kJ mol^{-1}]

37. Calculate the ionisation energy of (a) one Li^{2+} ion and (b) one mole of Li^{2+} ion. (Given, $R = 1.0974 \times 10^{-7}$ m^{-1})

[Ans. (a) 19.638×10^{-18} J (b) 1.118×10^4 kJ mol^{-1}]

38. A series of lines in the spectrum of atomic hydrogen lies at 656.46 nm, 486.27 nm, 439.17 nm and 410.29 nm. What is the wavelength of the next line in this series? What is the ionisation energy of the atom when it is in the lower state of transition?

[Ans. $\lambda_{next} = 397.15$ nm; IE = 3.40 eV]

39. A certain line of the Lyman series of hydrogen and a certain line of the Balmer series of He^+ ion have nearly the same wavelength. To what transition do they belong? Small differences between their Rydberg constant may be neglected.

[Ans.

Hydrogen	Helium
$2 \to 1$	$4 \to 2$
$3 \to 1$	$6 \to 2$
$4 \to 1$	$8 \to 2$]

40. What element has a hydrogen-like spectrum whose lines have wavelengths four times shorter than those of atomic hydrogen?

[Ans. He^+]

41. What lines of atomic hydrogen absorption spectrum fall within the wavelength ranges from 94.5 to 130 nm?
[**Ans.** 97.3; 102.6; 121.6 nm]

42. The binding energy of an electron in the ground state of an atom is equal to 24.6 eV. Find the energy required to remove both the electrons from the atom.
[**Ans.** 79 eV]

43. What is the ratio of the speeds of an electron in the first and second orbits of a hydrogen atom?
[**Ans.** 2 : 1]

44. Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit. **(IIT 1994)**
[**Ans.** 3]

45. The wave number of first line in Balmer series of hydrogen is $15200\ cm^{-1}$. What is the wave number of first line in Balmer series of Be^{3+}?
[**Ans.** $2.43 \times 10^5\ cm^{-1}$]

46. Calculate the speed of an electron in the ground state of hydrogen atom. What fraction of the speed of light is this value? How long does it take for the electron to complete one revolution around the nucleus? How many times does the electron travel around the nucleus in one second?
[**Ans.** $2.186 \times 10^6\ ms^{-1}; 7.29 \times 10^{-3}$]

47. An electron, in a hydrogen atom, in its ground state absorbs 1.5 times as much energy as the minimum required for its escape (*i.e.*, 13.6 eV) from the atom. Calculate the value of λ for the emitted electron.
[**Ans.** 4.69 Å]

48. The radius of the fourth orbit of hydrogen is 0.85 nm. Calculate the velocity of an electron in this orbit ($m_e = 9.1 \times 10^{-31}$ kg).
[**Ans.** $5.44 \times 10^5\ m\ sec^{-1}$]

49. A beam of electrons accelerated with 4.64 V was passed through a tube having mercury vapours. As a result of absorption, electronic changes occurred with mercury atoms and light was emitted. If the full energy of single electron was converted into light, what was the wave number of emitted light?
[**Ans.** $3.75 \times 10^4\ cm^{-1}$]

50. An electron jumps from an outer orbit to an inner orbit with the energy difference of 3.0 eV. What will be the wavelength of the line and in what region does the emission take place?
[**Ans.** $\lambda = 4140$ Å; visible region]
[**Hint:** $1\ eV = 1.6 \times 10^{-12}$ erg]

51. The first ionisation energy of a certain atom took place with an absorption of radiation of frequency 1.5×10^{18} cycle per second. Calculate its ionisation energy in calorie per gram atom.
[**Ans.** 1.43×10^8 cal]
[**Hint:** 1 calorie = 4.18×10^7 erg
Apply $E = h \times \nu \times$ Avogadro's number]

52. Find the wavelength associated with an electron which has mass 9.1×10^{-28} g and is moving with a velocity of 10^5 cm sec^{-1}. (Given $h = 6.625 \times 10^{-27}$ erg-sec)
[**Ans.** $\lambda = 7.28 \times 10^{-5}$ cm]

53. Calculate the momentum of the particle which has de Broglie wavelength 1 Å (10^{-10} m) and $h = 6.6 \times 10^{-34}$ J-sec.
[**Ans.** $6.6 \times 10^{-24}\ kg\ m\ sec^{-1}$]

54. The uncertainty of a particle in momentum is 3.3×10^{-2} kg ms^{-1}. Calculate the uncertainty in its position. ($h = 6.6 \times 10^{-34}$ J-sec)
[**Ans.** 3.1×10^{-14} m]

55. Calculate the product of uncertainties of displacement and velocity of a moving electron having a mass 9.1×10^{-28} g.
[**Ans.** $5.77 \times 10^{-5}\ m^2\ s^{-1}$]
[**Hint:** $\Delta x \cdot \Delta v \geq \dfrac{h}{4\pi m}$]

56. (a) A transition metal cation x^{3+} has magnetic moment $\sqrt{35}$ BM. What is the atomic number of x^{3+}?
(b) Select the coloured ion and the ion having maximum

1	1	1	1	1

magnetic moment (i) Fe^{2+}, (ii) Cu^{+}, (iii) Sc^{3+} and

(b) $Fe^{2+} \rightarrow$

1l	1	1	1	1

$Mn^{2+} \rightarrow$

1	1	1		

(iv) Mn^{2+}
[**Hint:** (a) 26, $_{26}Fe \rightarrow 3d^6 4s^2$
$Fe^{3+} \rightarrow 3d^5 4s^0$
$\mu = \sqrt{n(n+2)} = \sqrt{5 \times 7} = \sqrt{35}$
Both these ions will be coloured and magnetic moment of Fe^{2+} will be greater.]

57. A photon of wavelength 4000 Å strikes a metal surface, the work function of the metal being 2.13 eV. Calculate (i) energy of the photon in eV; (ii) kinetic energy of the emitted photoelectron and (iii) velocity of the photoelectron.
[**Ans.** $E = 3.10$ eV; KE = 0.97 eV; Velocity = $5.85 \times 10^5\ ms^{-1}$]
[**Hint:** $1\ eV = 1.602 \times 10^{-19}$ J]

58. Calculate the ratio between the wavelengths of an electron and a proton, if the proton is moving at half the velocity of the electron (mass of the proton = 1.67×10^{-27} kg; mass of the electron = 9.11×10^{-28} g).
[**Ans.** 9.2455×10^{-2} m]
[**Hint:** Apply de Broglie equation, $\lambda = \dfrac{h}{mv}$

$$\text{Wavelength of electron} = \frac{6.625 \times 10^{-34}}{9.11 \times 10^{-31} v}$$

$$\text{Wavelength of proton} = \frac{6.625 \times 10^{-34}}{1.67 \times 10^{-27} \times 0.5 v}\text{]}$$

59. A moving electron has 2.8×10^{-25} J of kinetic energy. Calculate its wavelength.
(Mass of electron = 9.1×10^{-31} kg)
[**Ans.** 9.2455×10^{-7} m]

[Hint: $v = \sqrt{\dfrac{2 \times \text{KE}}{m}} = 784.46\ \text{ms}^{-1}$; $\lambda = \dfrac{h}{mv}$]

60. Helium has mass number 4 and atomic number 2. Calculate the nuclear binding energy per nucleon (mass of neutron = 1.00893 amu and proton = 1.00814 amu, He = 4.0039 amu and mass of electron is negligible).

[Ans. 7.038 MeV]

61. Calculate the mass defect and binding energy per nucleon of $^{16}_{8}O$ which has a mass 15.99491 amu.

$$\begin{aligned} \text{Mass of neutron} &= 1.008655 \text{ amu} \\ \text{Mass of proton} &= 1.007277 \text{ amu} \\ \text{Mass of electron} &= 0.0005486 \text{ amu} \\ 1 \text{ amu} &= 931.5 \text{ MeV} \end{aligned}$$

[Ans. 7.976 MeV/nucleon]

62. The circumference of the second Bohr orbit of electron in the hydrogen atom is 600 nm. Calculate the potential difference to which the electron has to be subjected so that the electron stops. The electron had the de Broglie wavelength corresponding to the circumference.

[Hint: Number of waves 'n' = $\dfrac{\text{Circumference}}{\text{Wavelength}}$

$$n\lambda = 2\pi r$$
$$2\lambda = 600$$
$$\lambda = 300 \text{ nm}$$

Let stopping potential is V_0.

$$eV_0 = \frac{1}{2}mv^2 \quad \ldots \text{(i)}$$
$$\lambda = \frac{h}{mv}$$
$$v = \frac{h}{\lambda m} \quad \ldots \text{(ii)}$$

From equations (i) and (ii),

$$eV_0 = \frac{1}{2}m\left(\frac{h}{\lambda m}\right)^2$$
$$V_0 = \frac{h^2}{2m\lambda^2 e}$$
$$= \frac{(6.626 \times 10^{-34})^2}{2 \times (9.1 \times 10^{-31}) \times (300 \times 10^{-9})^2 \times 1.6 \times 10^{-19}}$$
$$= 1.675 \times 10^{-5} \text{ V}$$]

63. The velocity of an electron of mass 9.1×10^{-31} kg moving round the nucleus in the Bohr orbit (diameter of the orbit is 1.058 Å) is 2.2×10^{-6} m sec^{-1}. If momentum can be measured within the accuracy of 1%, then calculate uncertainty in position (Δx) of the electron.

[Ans. 2.64×10^3 metre]

64. An electron wave has wavelength 1 Å. Calculate the potential with which the electron is accelerated.

[Ans. 0.0826 volt]

65. Calculate the de Broglie wavelength associated with an α-particle having an energy of 7.7×10^{-13} J and a mass of 6.6×10^{-24} g. ($h = 6.6 \times 10^{-34}$ J-s)

[Ans. 6.56×10^{-13} cm]

66. An electron has mass 9.1×10^{-28} g and is moving with a velocity of 10^5 cm/sec. Calculate its kinetic energy and wavelength when $h = 6.626 \times 10^{-27}$ erg-sec.

[Ans. 4.55×10^{-8} erg; $\lambda = 7.28 \times 10^{-5}$ cm]

67. Calculate the de Broglie wavelengths of an electron and a proton having same kinetic energy of 100 eV.

[Ans. $\lambda_e = 123$ pm; $\lambda_p = 2.86$ pm]

68. Work function of sodium is 2.5 eV. Predict whether the wavelength 6500 Å is suitable for a photoelectron or not?

[Ans. No ejection]

69. Calculate the de Broglie wavelength associated with a helium atom in a helium gas sample at 27°C and 1 atm pressure.

[Ans. 7.3×10^{-11} metre]

70. The threshold frequency for a certain metal is 3.3×10^{14} cycle/sec. If incident light on the metal has a cut-off frequency 8.2×10^{14} cycle/sec, calculate the cut-off potential for the photoelectron.

[Ans. 2 volt]

71. Can you locate the electron within 0.005 nm?

[Ans. No.]

[Hint: Use uncertainty principle to determine uncertainty in velocity.

$$\Delta v \geq \frac{h}{4\pi m\, \Delta x}$$

On substitution, you will get,

$$\Delta v \geq 1.16 \times 10^7 \text{ ms}^{-1}$$

Velocity of electron is therefore expected to be as high as velocity of light. We may say that the velocity of electron is uncertain within 0.005 nm.]

72. The photoelectric cut-off voltage in a certain experiment is 1.5 volt. What is the maximum kinetic energy of the photoelectrons emitted?

[Ans. 2.4×10^{-19} joule]

73. A proton is accelerated to one-tenth the velocity of light. If its velocity can be measured with a precision of ±1%, what must be its uncertainty in position?
($h = 6.6 \times 10^{-34}$ J-s; mass of proton = 1.66×10^{-27} kg)

[Ans. 1.05×10^{-14} m]

74. In a photoelectric effect experiment, irradiation of a metal with light of frequency 5.2×10^{14} sec^{-1} yields electrons with maximum kinetic energy 1.3×10^{-19} J. Calculate the ν_0 of the metal.

[Ans. 3.2×10^{14} sec^{-1}]

75. Calculate the wavelength of a CO_2 molecule moving with a velocity of 440 m sec^{-1}.

[Ans. 2.06×10^{-11} metre]

76. The predominant yellow line in the spectrum of a sodium vapour lamp has a wavelength of 590 nm. What minimum accelerating potential is needed to excite this line in an electron tube having sodium vapours?

[Ans. 2.11 volt]

77. Find out the wavelength of a track star running a 100 metre dash in 10.1 sec, if its weight is 75 kg.

[**Ans.** 8.92×10^{-37} m]

78. At what velocity ratio are the wavelengths of an electron and a proton equal?

($m_e = 9.1 \times 10^{-28}$ g and $m_p = 1.6725 \times 10^{-24}$ g)

[**Ans.** $\frac{v_e}{v_p} = 1.8 \times 10^3$]

79. Through what potential difference must an electron pass to have a wavelength of 500 Å?

[**Ans.** 6.03×10^{-4} eV]

[**Hint:** Use $\lambda = \frac{h}{\sqrt{2\,eV\,m}}$]

80. Calculate the velocity of an α-particle which begins to reverse its direction at a distance of 2×10^{-14} m from a scattering gold nucleus ($Z = 79$).

[**Ans.** 2.346×10^7 m / sec]

81. Two hydrogen atoms collide head-on and end up with zero kinetic energy. Each then emits a photon with a wavelength 121.6 nm. Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before the collision? (Given, $R_H = 1.097 \times 10^7\,m^{-1}$ and $m_H = 1.67 \times 10^{-27}$ kg)

[**Ans.** $n_1 = 1$; $n_2 = 2$; 4.43×10^4 m sec^{-1}]

[**Hint:** Wavelength is in UV region; thus n_1 will be 1.

$$\frac{1}{121.6 \times 10^{-9}} = 1.097 \times 10^7 \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

$$n_2 = 2$$

$$\frac{1}{2}mv^2 = \frac{hc}{\lambda}$$

$$\frac{1}{2} \times 1.67 \times 10^{-27} \times v^2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{121.6 \times 10^{-9}}$$

$$v = 4.43 \times 10^4 \text{ m sec}^{-1}$$]

82. Show that the wavelength of electrons moving at a velocity very small compared to that of light and with a kinetic energy of V electron volt can be written as,

$$\lambda = \frac{12.268}{\sqrt{V}} \times 10^{-8} \text{ cm}$$

[**Hint:** Use the relation, $\lambda = \frac{h}{\sqrt{2Em}}$

Here, h = Planck's constant

$m = 9.1 \times 10^{-28}$ g (mass of e^-)

E = Kinetic energy of electron

$= V$ eV $= V \times 1.6 \times 10^{-12}$ erg]

83. What is the distance of closest approach to the nucleus of an α-particle which undergoes scattering by 180° in Geiger-Marsden experiment?

[**Ans.** $r_0 = 4.13$ fm]

[**Hint:** For closest approach,

$$\frac{1}{2}mv^2 = K\frac{Ze \times e}{r_0}$$

For Rutherford experiment,

$$\frac{1}{2}mv^2 = 5.5 \text{ MeV} = 5.5 \times 10^6 \times 1.6 \times 10^{-19} \text{ J} = 8.8 \times 10^{-13} \text{ J}$$

$$8.8 \times 10^{-13} = \frac{9 \times 10^9 \times 2 \times 79 \times (1.6 \times 10^{-19})^2}{r_0}$$

$$r_0 = 4.136 \times 10^{-15} \text{ m}$$

$$r_0 = 4.13 \text{ fm}$$]

84. Photoelectrons are liberated by ultraviolet light of wavelength 3000 Å from a metallic surface for which the photoelectric threshold is 4000 Å. Calculate de Broglie wavelength of electrons emitted with maximum kinetic energy.

[**Ans.** $\lambda = 1.2 \times 10^{-9}$ m]

[**Hint:**

KE = Quantum energy − Threshold energy

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3000 \times 10^{-10}} - \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}}$$

$$= 6.626 \times 10^{-19} - 4.9695 \times 10^{-19}$$

$$= 1.6565 \times 10^{-19} \text{ joule}$$

$$\frac{1}{2}mv^2 = 1.6565 \times 10^{-19}$$

$$m^2v^2 = 2 \times 1.6565 \times 10^{-19} \times 9.1 \times 10^{-31}$$

$$mv = 5.49 \times 10^{-25}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{5.49 \times 10^{-25}} = 1.2 \times 10^{-9} \text{ m}$$]

85. Show that de Broglie wavelength of electrons accelerated V volt is very nearly given by:

$$\lambda \text{ (in Å)} = \left(\frac{150}{V}\right)^{1/2}$$

[**Hint:** $\lambda = \frac{h}{\sqrt{2eVm}}$

$$\lambda = \left[\frac{h^2}{2eVm} \times 10^{20}\right]^{1/2} \text{Å}$$

$$= \left[\frac{(6.626 \times 10^{-34})^2 \times 10^{20}}{2 \times 1.6 \times 10^{-19} \times V \times 9.1 \times 10^{-31}}\right]^{1/2} = \left[\frac{150}{V}\right]^{1/2}$$]

86. A 1 MeV proton is sent against a gold leaf ($Z = 79$). Calculate the distance of closest approach for head-on collision.

[**Ans.** 1.137×10^{-13} m]

[**Hint:** $d = \frac{Ze^2}{4\pi\varepsilon_0(\frac{1}{2}mv^2)}$. Do like Q.No. 83]

87. What is the energy, momentum and wavelength of the photon emitted by a hydrogen atom when an electron makes a transition from $n = 2$ to $n = 1$? Given that ionization potential is 13.6 eV.

[**Ans.** 16.32×10^{-19} J, 5.44×10^{-27} kg m / sec, 1218 Å]

[**Hint:** $E_1 = -13.6$ eV

$$E_2 = \frac{-13.6}{4} \text{ eV}$$

$$\Delta E = \frac{3}{4} \times 13.6 \text{ eV}$$

$$= 0.75 \times 13.6 \times 1.6 \times 10^{-19} \text{ J} = 1.632 \times 10^{-18} \text{ J}$$

$$\frac{hc}{\lambda} = 1.632 \times 10^{-18}$$

$$\lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{1.632 \times 10^{-18}} = 1218 \times 10^{-10} \text{ m} = 1218 \text{ Å}$$

$$\lambda = \frac{h}{p}$$

$$\therefore \quad p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}}{1218 \times 10^{-10}} = 5.44 \times 10^{-27} \text{ kg-m/sec}]$$

88. Calculate the orbital angular momentum of the following orbitals:

(a) $3p$ (b) $3d$ (c) $3s$

[**Ans.** (a) $\sqrt{2}\hbar$ (b) $\sqrt{6}\hbar$ (c) 0]

[**Hint:** (a) $\mu_l = \sqrt{l(l+1)}\,\frac{h}{2\pi}$ for $3p$, $l = 1 = \sqrt{2}\,\hbar$

(b) $\mu_l = \sqrt{6}\,\hbar$ for $3d$, $l = 2$

(c) $\mu_l = 0$ for $3s$, $l = 0$]

89. A single electron system has ionization energy 11180 kJ mol^{-1}. Find the number of protons in the nucleus of the system.

[**Ans.** $Z = 3$]

[**Hint:**
$$\text{IE} = \frac{Z^2}{n^2} \times 21.69 \times 10^{-19} \text{ J}$$

$$\frac{11180 \times 10^3}{6.023 \times 10^{23}} = \frac{Z^2}{1^2} \times 21.69 \times 10^{-19}$$

$$Z \approx 3]$$

90. Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda = 550$ nm) are needed to generate this minimum amount of energy?

[**Ans.** 28]

91. How many hydrogen atoms in the ground state are excited by means of monochromatic radiation of wavelength 970.6 Å. How many different lines are possible in the resulting emission spectrum? Find the longest wavelength among these.

[**Ans.** Six different lines, $\lambda = 1215.6$ Å]

[**Hint:**
$$E_n - E_1 = \frac{hc}{\lambda}$$

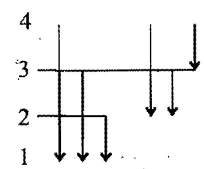
$$\frac{-21.69 \times 10^{-19}}{n^2} + \frac{21.69 \times 10^{-19}}{1} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{970.6 \times 10^{-10}}$$

$n \approx 4$

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = 109677.77 \times 1^2\left(\frac{1}{1^2} - \frac{1}{4}\right)$$

$\lambda = 1215.68$ Å]



six different lines

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. The ratio of e/m for a cathode ray:
(a) varies with a gas in a discharge tube
(b) is fixed
(c) varies with different electrodes
(d) is maximum if hydrogen is taken
2. Which of the following statements is wrong about cathode rays?
(a) They travel in straight lines towards cathode
(b) They produce heating effect
(c) They carry negative charge
(d) They produce X-rays when strike with material having high atomic masses
3. Cathode rays are:
(a) electromagnetic waves (b) stream of α-particles
(c) stream of electrons (d) radiations
4. Cathode rays have:
(a) mass only (b) charge only
(c) no mass and no charge (d) mass and charge both
5. Which is the correct statement about proton?
(a) It is a nucleus of deuterium
(b) It is an ionised hydrogen molecule
(c) It is an ionised hydrogen atom
(d) It is an α-particle
6. Neutron was discovered by:
(a) J.J. Thomson (b) Chadwick
(c) Rutherford (d) Priestley
7. The discovery of neutron came very late because:
(a) it is present in nucleus
(b) it is a fundamental particle
(c) it does not move
(d) it does not carry any charge
8. The fundamental particles present in equal numbers in neutral atoms (atomic number 71) are:
(a) protons and electrons (b) neutrons and electrons
(c) protons and neutrons (d) protons and positrons
9. The nucleus of the atom consists of:
(a) protons and neutrons
(b) protons and electrons
(c) neutrons and electrons
(d) protons, neutrons and electrons
10. The absolute value of charge on the electron was determined by:
(a) J.J. Thomson (b) R.A. Millikan
(c) Rutherford (d) Chadwick
11. Atomic number of an element represents: **(CBSE 1990)**
(a) number of neutrons in the nucleus
(b) atomic mass of an element
(c) valency of an element
(d) number of protons in the nucleus
12. Rutherford's experiment on scattering of α-particles showed for the first time that the atom has: **[CMC (Vellore) 1991]**
(a) electrons (b) protons (c) neutrons (d) nucleus
13. Rutherford's scattering experiment is related to the size of the:
(a) nucleus (b) atom (c) electron (d) neutron
14. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because:
(a) alpha particles are much heavier than electrons
(b) alpha particles are positively charged
(c) most part of the atom is empty space
(d) alpha particles move with very high velocity
15. The radius of an atomic nucleus is of the order of: **[PMT (MP) 1991]**
(a) 10^{-10} cm (b) 10^{-13} cm
(c) 10^{-15} cm (d) 10^{-8} cm
16. Atomic size is of the order of:
(a) 10^{-8} cm (b) 10^{-10} cm (c) 10^{-13} cm (d) 10^{-6} cm
17. Atoms may be regarded as comprising of protons, neutrons and electrons. If the mass attributed by electrons was doubled and that attributed by neutrons was halved, the atomic mass of ^{12}C would be:
(a) approximately the same (b) doubled
(c) reduced approx. 25% (d) approx. halved
18. Positive ions are formed from neutral atoms by the loss of:
(a) neutrons (b) protons
(c) nuclear charge (d) electrons
19. The nitrogen atom has 7 protons and 7 electrons. The nitride ion will have:
(a) 10 protons and 7 electrons
(b) 7 protons and 10 electrons
(c) 4 protons and 7 electrons
(d) 4 protons and 10 electrons
20. A light whose frequency is equal to 6×10^{14} Hz is incident on a metal whose work function is 2eV ($h = 6.63\times10^{-34}$ Js, $1\text{eV} = 1.6\times10^{-19}$ J). The maximum energy of electrons emitted will be: **(VITEEE 2008)**
(a) 2.49 eV (b) 4.49 eV (c) 0.49 eV (d) 5.49 eV
[**Hint:** Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

Absorbed energy = $h\nu$
$$= 6.626\times10^{-34}\times6\times10^{14}$$
$$= 3.9756\times10^{-19}\ \text{J}$$
$$= \frac{3.9756\times10^{-19}}{1.6\times10^{-19}} = 2.49\ \text{eV}$$
$$2.49 = 2\ \text{eV} + \text{Kinetic energy of photoelectron}$$
Kinetic energy of photoelectron = 0.49 eV]
21. The size of the nucleus is measured in:
(a) amu (b) angstrom
(c) cm (d) fermi
22. The highest value of e/m of anode rays has been observed when the discharge tube is filled with:
(a) nitrogen (b) oxygen (c) hydrogen (d) helium

23. The particle with 13 protons and 10 electrons is:
(a) Al atom (b) Al^{3+} ion
(c) nitrogen isotope (d) none of these

24. Which of the following atoms contains the least number of neutrons?
(a) $^{235}_{92}U$ (b) $^{238}_{92}U$
(c) $^{239}_{93}Np$ (d) $^{240}_{93}Np$

25. The number of neutrons in dipositive zinc ion (Zn^{2+}, with mass number 70) is:
(a) 34 (b) 36 (c) 38 (d) 40

26. Which of the properties of the elements is a whole number?
(a) Atomic mass (b) Atomic number
(c) Atomic radius (d) Atomic volume

27. Increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and α-particle (α) is:
(a) e, p, n, α (b) n, p, e, α
(c) n, p, α, e (d) n, α, p, e

28. The mass of neutron is of the order of:
(a) 10^{-27} kg (b) 10^{-26} kg
(c) 10^{-25} kg (d) 10^{-24} kg

29. The atoms of various isotopes of a particular element differ from each other in the number of:
(a) electrons in the outer shell only
(b) protons in the nucleus
(c) electrons in the inner shell only
(d) neutrons in the nucleus

30. Isotopes of the same element have:
(a) same number of neutrons
(b) same number of protons
(c) same atomic mass
(d) different chemical properties

31. Which of the following conditions is incorrect for a well behaved wave function (ψ)? **[EAMCET (Engg.) 2010]**
(a) ψ must be finite (b) ψ must be single valued
(c) ψ must be infinite (d) ψ must be continuous

32. Atomic mass of an element is not a whole number because:
(a) it contains electrons, protons and neutrons
(b) it contains isotopes
(c) it contains allotropes
(d) all of the above

33. Nucleons are:
(a) protons and neutrons
(b) neutrons and electrons
(c) protons and electrons
(d) protons, neutrons and electrons

34. Isotopes of an element have:
(a) different chemical and physical properties
(b) similar chemical and physical properties
(c) similar chemical but different physical properties
(d) similar physical and different chemical properties

35. Isotopes are identified by:
(a) positive ray analysis
(b) Astons' mass spectrograph
(c) Dempster's mass spectrograph
(d) all of the above

36. Mass spectrograph helps in the detection of isotopes because they:
(a) have different atomic masses
(b) have same number of electrons
(c) have same atomic number
(d) have same atomic masses

37. Which of the following statements is incorrect?
(a) The charge on an electron and proton are equal and opposite
(b) Neutrons have no charge
(c) Electrons and protons have the same mass
(d) The mass of a proton and a neutron are nearly the same

38. The charge on positron is equal to the charge on:
(a) proton (b) electron
(c) α-particle (d) neutron

39. Discovery of the nucleus of an atom was due to the experiment carried out by:
(a) Bohr (b) Rutherford
(c) Moseley (d) Thomson

40. Isobars are the atoms of: **(CBSE 1991)**
(a) same elements having same atomic number
(b) same elements having same atomic mass
(c) different elements having same atomic mass
(d) none of the above

41. Which of the following pairs represents isobars?
(a) $^{3}_{2}He$ and $^{4}_{2}He$ (b) $^{24}_{12}Mg$ and $^{25}_{12}Mg$
(c) $^{40}_{19}K$ and $^{40}_{20}Ca$ (d) $^{40}_{19}K$ and $^{39}_{19}K$

42. Na^+ ion is isoelectronic with: **(CPMT 1990)**
(a) Li^+ (b) Mg^{2+} (c) Ca^{2+} (d) Ba^{2+}

43. The triad of nuclei that is isotonic is:
(a) $^{14}_{6}C$, $^{14}_{7}N$, $^{19}_{9}F$ (b) $^{12}_{6}C$, $^{14}_{7}N$, $^{19}_{9}F$
(c) $^{14}_{6}C$, $^{14}_{7}N$, $^{17}_{9}F$ (d) $^{14}_{6}C$, $^{15}_{7}N$, $^{17}_{9}F$

44. Sodium atoms and sodium ions:
(a) are chemically similar
(b) both react vigorously with water
(c) have same number of electrons
(d) have same number of protons

45. In $^{35}_{17}Cl$ and $^{37}_{17}Cl$, which of the following is false?
(a) Both have 17 protons
(b) Both have 17 electrons
(c) Both have 18 neutrons
(d) Both show same chemical properties

46. Which of the following is isoelectronic with neon?
(a) O^{2-} (b) F^+ (c) Mg (d) Na

47. Neutrino has:
(a) charge +1, mass 1 (b) charge 0, mass 0
(c) charge −1, mass 1 (d) charge 0, mass 1

48. Positronium is the name given to an atom-like combination formed between: **(JIPMER 1991)**
(a) a positron and a proton
(b) a positron and a neutron

(c) a positron and an α-particle
(d) a positron and an electron

49. An isotone of $^{76}_{32}Ge$ is:
(a) $^{77}_{32}Ge$ (b) $^{78}_{33}As$ (c) $^{77}_{34}Se$ (d) $^{78}_{34}Se$

50. Which of the following does not characterise X-rays? **(IIT 1992)**
(a) The radiations can ionise gases
(b) It causes ZnS to fluorescence
(c) Deflected by electric and magnetic fields
(d) Have wavelengths shorter than ultraviolet rays

51. X-rays are produced when a stream of electrons in an X-ray tube:
(a) hits the glass wall of the tube
(b) strikes the metal target
(c) passes through a strong magnetic field
(d) none of the above

52. Radius of a nucleus is proportional to:
(a) A (b) $A^{1/3}$ (c) A^2 (d) $A^{2/3}$

53. The nature of positive rays produced in a vacuum discharge tube depends upon:
(a) the nature of the gas filled
(b) nature of the material of cathode
(c) nature of the material of anode
(d) the potential applied across the electrodes

54. Electromagnetic radiation with maximum wavelength is: **(MLNR 1991)**
(a) ultraviolet (b) radiowaves
(c) X-rays (d) infrared

55. The ratio of energy of radiations of wavelengths 2000 Å and 4000 Å is: **(CBSE 1994)**
(a) 2 (b) 4 (c) 1/2 (d) 1/4

56. The ratio of the diameter of the atom and the diameter of the nucleus is:
(a) 10^5 (b) 10^3 (c) 10 (d) 10^{-1}

57. The ratio of the volume of the atom and the volume of the nucleus is:
(a) 10^{10} (b) 10^{12} (c) 10^{15} (d) 10^{20}

58. Which of the following statements is incorrect?
(a) The frequency of radiation is inversely proportional to its wavelength
(b) Energy of radiation increases with increase in frequency
(c) Energy of radiation decreases with increase in wavelength
(d) The frequency of radiation is directly proportional to its wavelength

59. Visible light consists of rays with wavelengths in the approximate range of:
(a) 4000 Å to 7500 Å
(b) 4×10^{-3} cm to 7.5×10^{-4} cm
(c) 4000 nm to 7500 nm
(d) 4×10^{-5} m to 7.5×10^{-6} m

60. Which of the following statements concerning light is false?
(a) It is a part of the electromagnetic spectrum
(b) It travels with same velocity, *i.e.*, 3×10^{10} cm/s
(c) It cannot be deflected by a magnet
(d) It consists of photons of same energy

61. A 600 W mercury lamp emits monochromatic radiation of wavelength 331.3 nm. How many photons are emitted from the lamp per second ? **[PET (Kerala) 2010]**
($h = 6.626\times10^{-34}$ Js, velocity of light $= 3\times10^8$ ms^{-1})
(a) 1×10^{19} (b) 1×10^{20}
(c) 1×10^{21} (d) 1×10^{23}
(e) 1×10^{22}

[**Hint :** Power $= \dfrac{\text{Energy}}{\text{Time}}$

$$600 = \frac{nhc}{\lambda\times 1\text{ sec}}$$

$$600 = \frac{n\times6.626\times10^{-34}\times3\times10^8}{331.3\times10^{-9}}$$

$$n = 1\times10^{21}]$$

62. Out of X-rays, visible, ultraviolet, radiowaves, the largest frequency is of:
(a) X-rays (b) visible
(c) ultraviolet (d) radiowaves

63. The wave number which corresponds to electromagnetic radiations of 600 nm is equal to:
(a) 1.6×10^4 cm^{-1} (b) 0.16×10^4 cm^{-1}
(c) 16×10^4 cm^{-1} (d) 160×10^4 cm^{-1}

64. Line spectrum is characteristic of:
(a) molecules (b) atoms
(c) radicals (d) none of these

65. Which one of the following is not the characteristic of Planck's quantum theory of radiation? **(AIIMS 1991)**
(a) The energy is not absorbed or emitted in whole number multiple of quantum
(b) Radiation is associated with energy
(c) Radiation energy is not emitted or absorbed continuously but in the form of small packets called quanta
(d) This magnitude of energy associated with a quantum is proportional to the frequency

66. Which of the following among the visible colours has the minimum wavelength?
(a) Red (b) Blue
(c) Green (d) Violet

67. The spectrum of helium is expected to be similar to that of:
(a) H (b) Na (c) He^+ (d) Li^+

68. According to classical theory if an electron is moving in a circular orbit around the nucleus:
(a) it will continue to do so for sometime
(b) its orbit will continuously shrink
(c) its orbit will continuously enlarge
(d) it will continue to do so for all the time

69. Bohr advanced the idea of:
(a) stationary electrons (b) stationary nucleus
(c) stationary orbits (d) elliptical orbits

70. On Bohr stationary orbits:
(a) electrons do not move
(b) electrons move emitting radiations
(c) energy of the electron remains constant
(d) angular momentum of the electron is $\dfrac{h}{2\pi}$

71. Energy of Bohr orbit: **(DPMT 1991)**
(a) increases as we move away from the nucleus
(b) decreases as we move away from the nucleus
(c) remains the same as we move away from the nucleus
(d) none of the above

72. Which of the following statements does not form part of Bohr's model of the hydrogen atom?
(a) Energy of the electron in the orbit is quantized
(b) The electron in the orbit nearest to the nucleus has the lowest energy
(c) Electrons revolve in different orbit nucleus
(d) The position and velocity of the electron in the orbit cannot be determined simultaneously

73. Which of the following statements does not form a part of Bohr's model of hydrogen atom? **(DCE 2005)**
(a) Energy of the electrons in the orbit is quantised
(b) The electron in the orbit nearest to the nucleus has the lowest energy
(c) Electrons revolve in different orbits around the nucleus
(d) The position and velocity of the electrons in the orbit cannot be determined simultaneously

74. The radius of the first orbit of H-atom is r. Then the radius of the first orbit of Li^{2+} will be: **[AMU-PMT 2009]**
(a) $\frac{r}{9}$ (b) $\frac{r}{3}$ (c) $3r$ (d) $9r$

[Hint : $r = \frac{n^2}{z} \times 0.529\text{Å}$]

75. The energy liberated when an excited electron returns to its ground state can have:
(a) any value from zero to infinity
(b) only negative values
(c) only specified positive values
(d) none of the above

76. On the basis of Bohr's model, the radius of the 3rd orbit is:
(a) equal to the radius of first orbit
(b) three times the radius of first orbit
(c) five times the radius of first orbit
(d) nine times the radius of first orbit

77. The ratio of 2nd, 4th and 6th orbits of hydrogen atom is:
(a) 2 : 4 : 6 (b) 1 : 4 : 9
(c) 1 : 4 : 6 (d) 1 : 2 : 3

78. Which point does not pertain to Bohr's model of atom?
(a) Angular momentum is an integral multiple of $h/(2\pi)$
(b) The path of the electron is circular
(c) Force of attraction towards nucleus = centrifugal force
(d) The energy changes are taking place continuously

79. The distance between 3rd and 2nd orbits in the hydrogen atom is:
(a) 2.646×10^{-8} cm (b) 2.116×10^{-8} cm
(c) 1.058×10^{-8} cm (d) 0.529×10^{-8} cm

80. The correct expression derived for the energy of an electron in the nth energy level in hydrogen atom is:
(a) $E_n = \frac{2\pi^2 me^4}{n^2h^2}$ (b) $E_n = -\frac{2\pi^2 me^4}{nh^2}$
(c) $E_n = -\frac{2\pi me^2}{n^2h^2}$ (d) $E_n = -\frac{2\pi^2 me^4}{n^2h^2}$

81. According to Bohr theory, the angular momentum for an electron of 5th orbit is:
(a) $5h/\pi$ (b) $2.5h/\pi$ (c) $5\pi/h$ (d) $25h/\pi$

82. The value of Bohr radius of hydrogen atom is: **(CBSE 1991)**
(a) 0.529×10^{-7} cm (b) 0.529×10^{-8} cm
(c) 0.529×10^{-9} cm (d) 0.529×10^{-10} cm

83. The energy of an electron in the nth Bohr orbit of hydrogen atom is: **(CBSE 1992)**
(a) $-\frac{13.6}{n^4}$ eV (b) $-\frac{13.6}{n^3}$ eV (c) $-\frac{13.6}{n^2}$ eV (d) $-\frac{13.6}{n}$ eV

84. Which of the following electron transitions in hydrogen atom will require largest amount of energy? **(MLNR 1992)**
(a) from $n = 1$ to $n = 2$ (b) from $n = 2$ to $n = 3$
(c) from $n = \infty$ to $n = 1$ (d) from $n = 3$ to $n = 5$

85. For a hydrogen atom, the energies that an electron can have are given by the expression, $E = -13.58/n^2$ eV, where n is an integer. The smallest amount of energy that a hydrogen atom in the ground state can absorb is:
(a) 1.00 eV (b) 3.39 eV (c) 6.79 eV (d) 10.19 eV

86. The energy of hydrogen atom in its ground state is -13.6 eV. The energy of the level corresponding to $n = 5$ is: **(CBSE 1990)**
(a) -0.54 eV (b) -5.40 eV (c) -0.85 eV (d) -2.72 eV

87. $E_n = -313.6/n^2$ kcal/mol. If the value of $E = -34.84$ kcal/mol, to which value does 'n' correspond?
(a) 4 (b) 3 (c) 2 (d) 1

88. The ratio of the difference between 1st and 2nd Bohr orbits energy to that between 2nd and 3rd orbits energy is:
(a) 1/2 (b) 1/3 (c) 27/5 (d) 5/27

89. Bohr's model can explain:
(a) spectrum of hydrogen atom only
(b) spectrum of any atom or ion having one electron only
(c) spectrum of hydrogen molecule
(d) solar spectrum

90. The energy difference between two electronic states is 43.56 kcal/mol. The frequency of light emitted when the electron drops from higher orbit to lower orbit, is:
(Planck's constant = 9.52×10^{-14} kcal/mol)
(a) 9.14×10^{14} cycle/sec (b) 45.7×10^{14} cycle/sec
(c) 91.4×10^{14} cycle/sec (d) 4.57×10^{14} cycle/sec

91. Which of the following transitions of an electron in hydrogen atom emits radiation of the lowest wavelength? **[EAMCET (Engg.) 2010]**
(a) $n_2 = \infty$ to $n_1 = 2$ (b) $n_2 = 4$ to $n_1 = 3$
(c) $n_2 = 2$ to $n_1 = 1$ (d) $n_2 = 5$ to $n_1 = 3$

92. The wavelength of a spectral line for an electronic transition is inversely related to:
(a) number of electrons undergoing transition
(b) the nuclear charge of the atom
(c) the velocity of an electron undergoing transition
(d) the difference in the energy levels involved in the transition

93. The ionisation energy of the electron in the 1s-orbital of the hydrogen atom is 13.6 eV. The energy of the electron after promotion to 2s-orbital is: **[ISC (Bihar) 1993]**
(a) –3.4 eV (b) –13.6 eV
(c) –27.2 eV (d) 0.0 eV

94. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit it?
(a) 1s (b) 2s (c) 3s (d) 4s

95. The spectral lines corresponding to the radiation emitted by an electron jumping from 6th, 5th and 4th orbits to second orbit belong to:
(a) Lyman series (b) Balmer series
(c) Paschen series (d) Pfund series

96. The spectral lines corresponding to the radiation emitted by an electron jumping from higher orbits to first orbit belong to:
(a) Paschen series (b) Balmer series
(c) Lyman series (d) None of these

97. In a hydrogen atom, the transition takes place from $n = 3$ to $n = 2$. If Rydberg constant is $1.097 \times 10^7\ m^{-1}$, the wavelength of the emitted radiation is:
(a) 6564 Å (b) 6064 Å
(c) 6664 Å (d) 5664 Å

[**Hint:** Apply $\frac{1}{\lambda} = R\left[\frac{1}{x^2} - \frac{1}{y^2}\right]$]

98. The speed of the electron in the 1st orbit of the hydrogen atom in the ground state is (c is the velocity of light):
(a) $\frac{c}{1.37}$ (b) $\frac{c}{1370}$ (c) $\frac{c}{13.7}$ (d) $\frac{c}{137}$

[**Hint:** Velocity of electron in the 1st orbit, $v = h/(2\pi mr)$ $= 2.189 \times 10^8$ cm/sec.; velocity of light, $c = 3 \times 10^{10}$ cm/sec. Ratio $c/v = 137$]

99. Find the value of wave number $\bar{\nu}$ in terms of Rydberg's constant, when transition of electron takes place between two levels of He^+ ion whose sum is 4 and difference is 2.
(a) $\frac{8R}{9}$ (b) $\frac{32R}{9}$
(c) $\frac{3R}{4}$ (d) None of these

[**Hint :** $n_1 + n_2 = 4$, $n_2 - n_1 = 2$ $\therefore$ $n_1 = 1, n_2 = 3$

$$\bar{\nu} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$= R \times 2^2\left[\frac{1}{1} - \frac{1}{3^2}\right] = \frac{32R}{9}$$]

100. With the increasing principal quantum number, the energy difference between adjacent energy levels in hydrogen atom:
(a) increases (b) decreases
(c) is the same (d) none of these

101. An electron in an atom: **[CEET (Bihar) 1992]**
(a) moves randomly around the nucleus
(b) has fixed space around the nucleus
(c) is stationary in various energy levels
(d) moves around its nucleus in definite energy levels

102. The wave number of first line of Balmer series of hydrogen is $15200\ cm^{-1}$. The wave number of the first Balmer line of Li^{2+} ion is: **[IIT (Screening) 1992]**
(a) 15,200 cm^{-1} (b) 60,800 cm^{-1}
(c) 76,000 cm^{-1} (d) 1,36,800 cm^{-1}

103. "The position and the velocity of a small particle like electron cannot be simultaneously determined." This statement is:
(a) Heisenberg uncertainty principle
(b) Pauli's exclusion principle
(c) aufbau's principle
(d) de Broglie's wave nature of the electron

104. de Broglie equation describes the relationship of wavelength associated with the motion of an electron and its:
(a) mass (b) energy (c) momentum (d) charge

105. If the magnetic quantum number of a given atom is represented by –3, then what will be its principal quantum number? **[BHU (Pre.) 2005]**
(a) 2 (b) 3 (c) 4 (d) 5

106. Which of the following relates to photons both as wave motion and as a stream of particles? **(IIT 1992)**
(a) Interference (b) Diffraction
(c) $E = h\nu$ (d) $E = mc^2$

107. If uncertainty in the position of an electron is zero, the uncertainty in its momentum would be:
(a) zero (b) $< h/(4\pi)$
(c) $> h/(4\pi)$ (d) infinite

108. Which one of the following explains light both as a stream of particles and as wave motion?
(a) Diffraction (b) $\lambda = h/p$
(c) Interference (d) Photoelectric effect

109. A body of mass x kg is moving with velocity of 100 m sec^{-1}. Its de Broglie wavelength is 6.62×10^{-35} m. Hence x is: ($h = 6.62 \times 10^{-34}$ J sec) **[CET (Karnataka) 2009]**
(a) 0.25 kg (b) 0.15 kg
(c) 0.2 kg (d) 0.1 kg

110. A 200 g cricket ball is thrown with a speed of 3.0×10^3 cm sec^{-1}. What will be its de Broglie's wavelength? ($h = 6.6 \times 10^{-27}$ g cm^2 sec^{-1}) **[CET (Gujarat) 2008]**
(a) 1.1×10^{-32} cm (b) 2.2×10^{-32} cm
(c) 0.55×10^{-32} cm (d) 11.0×10^{-32} cm

111. The electronic configuration of a dipositive ion M^{2+} is 2, 8, 14 and its atomic mass is 56. The number of neutrons in the nucleus would be:
(a) 30 (b) 32 (c) 34 (d) 42

112. An element with atomic number 20 will be placed in which period of the periodic table?
(a) 5th (b) 4th (c) 3rd (d) 2nd

113. The frequency of radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (Given ionisation energy of $H = 2.18 \times 10^{-18}$ J $atom^{-1}$ and $h = 6.626 \times 10^{-34}$ Js): **[Manipal (Med.) 2007]**
(a) $1.54 \times 10^{15}\ s^{-1}$ (b) $1.03 \times 10^{15}\ s^{-1}$
(c) $3.08 \times 10^{15}\ s^{-1}$ (d) $2 \times 10^{15}\ s^{-1}$

114. In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields? **(AIEEE 2005)**
(i) $n = 1, l = 0, m = 0$ (ii) $n = 2, l = 0, m = 0$

(iii) $n = 2, l = 1, m = 1$ (iv) $n = 3, l = 2, m = 1$
(v) $n = 3, l = 2, m = 0$
(a) (i) and (ii) (b) (ii) and (iii)
(c) (iii) and (iv) (d) (iv) and (v)

115. Which of the ions is not having the configuration of Ne?
(a) Cl^- (b) F^- (c) Na^+ (d) Mg^{2+}

116. Which of the following has the maximum number of unpaired *d*-electrons? **(KCET 2008)**
(a) Ni^{3+} (b) Cu^+ (c) Zn^{2+} (d) Fe^{2+}

117. Which of the following expressions gives the de Broglie relationship? **[JEE (WB) 2008]**
(a) $p = \frac{h}{mv}$ (b) $\lambda = \frac{h}{mv}$
(c) $\lambda = \frac{h}{mp}$ (d) $\lambda m = \frac{h}{p}$

118. The principal quantum number of an atom is related to the: **(MLNR 1990)**
(a) size of the orbital
(b) orbital angular momentum
(c) spin angular momentum
(d) orientation of the orbital in space

119. The magnetic quantum is a number related to:
(a) size (b) shape
(c) orientation (d) spin

120. The principal quantum number represents: **(CPMT 1991)**
(a) shape of an orbital
(b) number of electrons in an orbit
(c) distance of electron from nucleus
(d) number of orbitals in an orbit

121. The quantum number not obtained from the Schrödinger's wave equation is: **(IIT 1990)**
(a) n (b) l (c) m (d) s

122. In a given atom, no two electrons can have the same values for all the four quantum numbers. This is called: **(CPMT 1990)**
(a) Hund's rule (b) Pauli's exclusion principle
(c) Uncertainty principle (d) aufbau principle

123. The atomic orbital is:
(a) the circular path of the electron
(b) elliptical shaped orbit
(c) three-dimensional field around nucleus
(d) the region in which there is maximum probability of finding an electron

124. If the ionization energy for hydrogen atom is 13.6 eV, then the ionization energy for He^+ ion should be: **[PMT (Haryana) 2004]**
(a) 13.6 eV (b) 6.8 eV
(c) 54.4 eV (d) 72.2 eV

125. Principal, azimuthal and magnetic quantum numbers are respectively related to:
(a) size, shape and orientation
(b) shape, size and orientation
(c) size, orientation and shape
(d) none of the above

126. Energy of electron in the H-atom is determined by :
(a) only n (b) both n and l
(c) n, l and m (d) all the four quantum numbers

127. Any *p*-orbital can accommodate up to: **(MLNR 1990)**
(a) 4 electrons
(b) 2 electrons with parallel spins
(c) 6 electrons
(d) 2 electrons with opposite spins

128. How many electrons can fit into the orbitals that comprise the 3rd quantum shell $n = 3$?
(a) 2 (b) 8 (c) 18 (d) 32

129. The total number of orbitals in a principal shell is:
(a) n (b) n^2 (c) $2n^2$ (d) $3n^2$

130. Two electrons in K-shell will differ in:
(a) principal quantum number
(b) spin quantum number
(c) azimuthal quantum number
(d) magnetic quantum number

131. Which one of the following orbitals has the shape of a baby-boother ?
(a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{z^2} (d) p_y

132. Which one of the following represents an impossible arrangement? **(AIEEE 2009)**

	n	l	m	s		n	l	m	s
(a)	3	2	−2	1/2	(b)	4	0	0	1/2
(c)	3	2	−3	1/2	(d)	5	3	0	1/2

133. Which of the following sets of quantum numbers is correct for an electron in 4*f*-orbital? **(AIEEE 2004)**
(a) $n = 4, l = 3, m = +4, s = +1/2$
(b) $n = 4, l = 4, m = -4, s = -1/2$
(c) $n = 4, l = 3, m = +1, s = +1/2$
(d) $n = 3, l = 2, m = -2, s = +1/2$

134. The correct quantum numbers of 3*p*-electrons are: **[PMT (Raj.) 2004]**
(a) $n = 3, l = 2, m = +2, s = +1/2$
(b) $n = 3, l = 1, m = -1, s = -1/2$
(c) $n = 3, l = -2, m = -2, s = +1/2$
(d) none of the above

135. In any subshell, the maximum number of electrons having same values of spin quantum number is :
(a) $\sqrt{l(l+1)}$ (b) $l + 2$
(c) $2l + 1$ (d) $4l + 2$

[**Hint :** Number of electrons with same spin
$= \frac{1}{2} \times$ Total no. of electrons
$= \frac{1}{2} \times 2(2l + 1) = (2l + 1)$]

136. Which of the following represents the correct set of four quantum numbers of a 4*d*-electron? **(MLNR 1992)**
(a) 4, 3, 2, +1/2 (b) 4, 2, 1, 0
(c) 4, 3, −2, +1/2 (d) 4, 2, 1, −1/2

137. Values of magnetic orbital quantum number for an electron of M-shell can be : **[PET (Raj.) 2008]**
(a) 0, 1, 2 (b) −2, −1, 0, +1, +2
(c) 0, 1, 2, 3 (d) −1, 0, +1

138. Correct set of four quantum numbers for the outermost electron of rubidium ($Z = 37$) is:

(a) 5, 0, 0, 1/2 (b) 5, 1, 0, 1/2
(c) 5, 1, 1, 1/2 (d) 6, 0, 0, 1/2

139. Which one of the following subshells is spherical in shape?
(a) $4s$ (b) $4p$ (c) $4d$ (d) $4f$

140. In hydrogen atom, the electron is at a distance of 4.768 Å from the nucleus. The angular momentum of the electron is : **[EAMCET (Med.) 2010]**
(a) $\frac{3h}{2\pi}$ (b) $\frac{h}{2\pi}$
(c) $\frac{h}{\pi}$ (d) $\frac{3h}{\pi}$

[**Hint :** $r = \frac{n^2}{z} \times 0.529$ Å

$4.768 = \frac{n^2}{1} \times 0.529$

$n = 3$

$\therefore$ Angular momentum $(mvr) = \frac{nh}{2\pi} = \frac{3h}{2\pi}$]

141. Total number of m values for $n = 4$ is:
(a) 8 (b) 16 (c) 12 (d) 20

142. What is the total number of orbitals in the shell to which the g-subshell first arise?
(a) 9 (b) 16 (c) 25 (d) 36
[**Hint :** For g-subshell, $l = 4$
$\therefore$ It will arise in 5th shell.
Total number of orbitals in 5th shell $= n^2 = 25$]

143. In Bohr's model, if the atomic radius of the first orbit r_1, then radius of fourth orbit will be : **[BHU (Screening) 2010]**
(a) $4r_1$ (b) $6r_1$ (c) $16r_1$ (d) $\frac{r_1}{16}$

144. Which of the following statements is not correct for an electron that has quantum numbers $n = 4$ and $m = 2$? **(MLNR 1993)**
(a) The electron may have the q. no. $l = +1/2$
(b) The electron may have the q. no. $l = 2$
(c) The electron may have the q. no. $l = 3$
(d) The electron may have the q. no. $l = 0, 1, 2, 3$

145. The angular momentum of an electron depends on:
(a) principal quantum number
(b) azimuthal quantum number
(c) magnetic quantum number
(d) all of the above

146. The correct set of quantum numbers for the unpaired electron of a chlorine atom is: **(DPMT 2009)**
(a) $2, 0, 0, +\frac{1}{2}$ (b) $2, 1, -1, +\frac{1}{2}$
(c) $3, 1, -1, \pm\frac{1}{2}$ (d) $3, 0, 0, \pm\frac{1}{2}$

147. The magnetic quantum number for valency electron of sodium atom is:
(a) 3 (b) 2 (c) 1 (d) zero

148. The shape of the orbital is given by: **[PET (Raj.) 2008]**
(a) spin quantum number
(b) magnetic quantum number
(c) azimuthal quantum number
(d) principal quantum number

149. The energy of an electron of $2p_y$ orbital is:
(a) greater than $2p_x$ orbital
(b) less than $2p_z$ orbital
(c) equal to $2s$ orbital
(d) same as that of $2p_x$ and $2p_z$ orbitals

150. The two electrons occupying the same orbital are distinguished by:
(a) principal quantum number
(b) azimuthal quantum number
(c) magnetic quantum number
(d) spin quantum number

151. The maximum number of electrons in a subshell is given by the expression: **(AIEEE 2009)**
(a) $4l + 2$ (b) $4l - 2$
(c) $2l + 1$ (d) $2n^2$

152. The electronic configuration of an atom/ion can be defined by which of the following?
(a) Aufbau principle
(b) Pauli's exclusion principle
(c) Hund's rule of maximum multiplicity
(d) All of the above

153. An electron has a spin quantum number +1/2 and a magnetic quantum number − 1. It cannot be present in:
(a) d-orbital (b) f-orbital (c) s-orbital (d) p-orbital

154. The value of azimuthal quantum number for electrons present in $4p$-orbitals is:
(a) 1
(b) 2
(c) any value between 0 and 3 except 1
(d) zero

155. For the energy levels in an atom which one of the following statements is correct?
(a) The $4s$ sub-energy level is at a higher energy than the $3d$ sub-energy level
(b) The M-energy level can have maximum of 32 electrons
(c) The second principal energy level can have four orbitals and contain a maximum of 8 electrons
(d) The 5th main energy level can have maximum of 50 electrons

156. A new electron enters the orbital when:
(a) $(n + l)$ is minimum (b) $(n + l)$ is maximum
(c) $(n + m)$ is minimum (d) $(n + m)$ is maximum

157. For a given value of n (principal quantum number), the energy of different subshells can be arranged in the order of:
(a) $f > d > p > s$ (b) $s > p > d > f$
(c) $f > p > d > s$ (d) $s > f > p > d$

158. After filling the $4d$-orbitals, an electron will enter in:
(a) $4p$ (b) $4s$ (c) $5p$ (d) $4f$

159. According to Aufbau principle, the correct order of energy of $3d$, $4s$ and $4p$-orbitals is: **[CET (J&K) 2006]**
(a) $4p < 3d < 4s$ (b) $4s < 4p < 3d$
(c) $4s < 3d < 4p$ (d) $3d < 4s < 4p$

160. Number of p-electrons in bromine atom is: **[PMT (Haryana) 2004]**
(a) 12 (b) 15
(c) 7 (d) 17

161. [Ar] $3d^{10}4s^1$ electronic configuration belongs to: **[PET (MP) 2008]**
(a) Ti (b) Tl (c) Cu (d) V

162. How many unpaired electrons are there in Ni^{2+} ? ($Z = 28$)
(a) Zero (b) 8 (c) 2 (d) 4

163. The electronic configuration of chromium (Z = 24) is: **[PMT (MP) 1993; BHU (Pre.) 2005]**
(a) [Ne] $3s^2 3p^6 3d^4 4s^2$ (b) [Ne] $3s^2 3p^6 3d^5 4s^1$
(c) [Ne] $3s^2 3p^6 3d^1 4s^2$ (d) [Ne] $3s^2 3p^6 4s^2 4p^4$

164. The number of d-electrons in Fe^{2+} (At. No. 26) is not equal to that of the: **(MLNR 1993)**
(a) p-electrons in Ne (At. No. 10)
(b) s-electrons in Mg (At. No. 12)
(c) d-electrons in Fe atom
(d) p-electrons in Cl^- ion (At. No. 17)

165. If the electronic structure of oxygen atom is written as

$1s^2, 2s^2$ $\overset{\longleftarrow 2p \longrightarrow}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{}}$; it would violate: **[ISC (Bihar) 1993]**

(a) Hund's rule
(b) Pauli's exclusion principle
(c) both Hund's and Pauli's principles
(d) none of the above

166. The orbital diagram in which 'aufbau principle' is violated, is:

	2s	← 2p →		
(a)	↑↓	↑↓	↑	
(b)	↑	↑↓	↑	↑
(c)	↑↓	↑	↑	↑
(d)	↑↓	↑↓	↑↓	↑

167. The manganese ($Z = 25$) has the outer configuration:

	4s	←		3p		→
(a)	↑↓	↑↓	↑	↑	↑	↑
(b)	↑↓	↑	↑	↑	↑	↑
(c)	↑↓	↑↓	↑↓	↑		
(d)		↑↓	↑↓	↑	↑	↑

168. Which of the following elements is represented by the electronic configuration?

← 2p →
2s ↑↓ | ↑↓ | ↑
1s ↑↓
↑↓

(a) Nitrogen (b) Fluorine
(c) Oxygen (d) Neon

169. The radial probability distribution curve obtained for an orbital wave function (ψ) has 3 peaks and 2 radial nodes. The valence electron of which one of the following metals does this wave function (ψ) correspond to ? **[EAMCET (Med.) 2010]**
(a) Co (b) Li (c) K (d) Na
[**Hint :** $Na_{11} \longrightarrow 1s^2, 2s^2 2p^6, \underbrace{3s^1}_{\text{Valence electron}}$
Number of radial node $= n - l - 1$ ($n = 3$)
$= 3 - 0 - 1 = 2$]

170. Krypton (At. No. 36) has the electronic configuration [A] $4s^2 3d^{10} 4p^6$. The 37th electron will go into which one of the following sub-levels?
(a) $4f$ (b) $4d$
(c) $3p$ (d) $5s$

171. An ion which has 18 electrons in the outermost shell is: **(CBSE 1990)**
(a) K^+ (b) Cu^+ (c) Cs^+ (d) Th^{4+}

172. Which of the following has non-spherical shell of electrons? **(IIT 1993)**
(a) He (b) B (c) Be (d) Li

173. Which one of the following sets of quantum numbers is not possible for an electron in the ground state of an atom with atomic number 19? **[PET (Kerala) 2006; CET (Karnataka) 2009]**
(a) $n = 2, l = 0, m = 0$ (b) $n = 2, l = 1, m = 0$
(c) $n = 3, l = 1, m = -1$ (d) $n = 3, l = 2, m = \pm 2$
(e) $n = 4, l = 0, m = 0$

174. Helium nucleus is composed of two protons and two neutrons. If the atomic mass is 4.00388, how much energy is released when the nucleus is constituted?
(Mass of proton = 1.00757, Mass of neutron = 1.00893)
(a) 283 MeV (b) 28.3 MeV
(c) 2830 MeV (d) 2.83 MeV

175. Binding energy per nucleon of three nuclei A, B and C are 5.5, 8.5 and 7.5 respectively. Which one of the following nuclei is most stable?
(a) A (b) C
(c) B (d) Cannot be predicted

176. The mass of ${}_3^7Li$ is 0.042 less than the mass of 3 protons and 4 neutrons. The binding energy per nucleon in ${}_3^7Li$ is: **(BHU 1992)**
(a) 5.6 MeV (b) 56 MeV (c) 0.56 MeV (d) 560 MeV

177. Meson was discovered by:
(a) Powell (b) Seaborg
(c) Anderson (d) Yukawa

178. In most stable elements, the number of protons and neutrons are:
(a) odd-odd (b) even-even
(c) odd-even (d) even-odd

179. Nuclear particles responsible for holding all nucleons together are:
(a) electrons (b) neutrons
(c) positrons (d) mesons

180. The introduction of a neutron into the nuclear composition of an atom would lead to a change in: **(MLNR 1995)**

(a) its atomic mass
(b) its atomic number
(c) the chemical nature of the atom
(d) number of the electron also

181. Which of the following has highest orbital angular momentum?
(a) $4s$ (b) $4p$ (c) $4d$ (d) $4f$

182. Which of the following has maximum number of unpaired electrons? **[PMT (Raj.) 2004; BHU (Pre.) 2005]**
(a) Fe^{3+} (b) Fe^{2+} (c) Co^{2+} (d) Co^{3+}

183. An electron is not deflected on passing through a certain region, because:
(a) there is no magnetic field in that region
(b) there is a magnetic field but velocity of the electron is parallel to the direction of magnetic field
(c) the electron is a chargeless particle
(d) none of the above

184. In Millikan's oil drop experiment, we make use of:
(a) Ohm's law (b) Ampere's law
(c) Stoke's law (d) Faraday's law

185. A strong argument for the particle nature of cathode rays is:
(a) they can propagate in vacuum
(b) they produce fluorescence
(c) they cast shadows
(d) they are deflected by electric and magnetic fields

186. As the speed of the electrons increases, the measured value of charge to mass ratio (in the relativistic units):
(a) increases
(b) remains unchanged
(c) decreases
(d) first increases and then decreases

187. Which of the following are true for cathode rays?
(a) It travels along a straight line
(b) It emits X-rays when strikes a metal
(c) It is an electromagnetic wave
(d) It is not deflected by magnetic field

188. Three isotopes of an element have mass numbers, M, $(M+1)$ and $(M+2)$. If the mean mass number is $(M+0.5)$ then which of the following ratios may be accepted for $M, (M+1), (M+2)$ in that order?
(a) $1:1:1$ (b) $4:1:1$
(c) $3:2:1$ (d) $2:1:1$

189. The radii of two of the first four Bohr orbits of the hydrogen atom are in the ratio 1 : 4. The energy difference between them may be:
(a) either 12.09 eV or 3.4 eV (b) either 2.55 eV or 10.2 eV
(c) either 13.6 eV or 3.4 eV (d) either 3.4 eV or 0.85 eV

190. Photoelectric emission is observed from a surface for frequencies ν_1 and ν_2 of the incident radiation ($\nu_1 > \nu_2$). If the maximum kinetic energies of the photoelectrons in the two cases are in the ratio $1:k$ then the threshold frequency ν_0 is given by:
(a) $\frac{\nu_2 - \nu_1}{k-1}$ (b) $\frac{k\nu_1 - \nu_2}{k-1}$ (c) $\frac{k\nu_2 - \nu_1}{k-1}$ (d) $\frac{\nu_2 - \nu_1}{k}$

191. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number +2 is:
(a) 3 (b) 4 (c) 2 (d) 1

192. A certain negative ion X^{2-} has in its nucleus 18 neutrons and 18 electrons in its extranuclear structure. What is the mass number of the most abundant isotope of X?
(a) 36 (b) 35.46 (c) 32 (d) 39

193. Which of the following statements is not correct?
(a) The shape of an atomic orbital depends on the azimuthal quantum number
(b) The orientation of an atomic orbital depends on the magnetic quantum number
(c) The energy of an electron in an atomic orbital of multielectron atom depends on the principal quantum number
(d) The number of degenerate atomic orbitals of one type depends on the values of azimuthal and magnetic quantum numbers

194. Gases begin to conduct electricity at low pressure because: **(CBSE 1994)**
(a) at low pressures gases turn to plasma
(b) colliding electrons can acquire higher kinetic energy due to increased mean free path leading to ionisation of atoms
(c) atoms break up into electrons and protons
(d) the electrons in atoms can move freely at low pressure

195. An electron of mass m and charge e, is accelerated from rest through a potential difference V in vacuum. Its final speed will be: **(CBSE 1994)**
(a) $\sqrt{(eV/m)}$ (b) $2eV/m$
(c) $\sqrt{(eV/2m)}$ (d) $\sqrt{(2eV/m)}$

196. The difference in angular momentum associated with the electron in the two successive orbits of hydrogen atom is:
(a) h/π (b) $h/2\pi$ (c) $h/2$ (d) $(n-1)h/2\pi$

197. Photoelectric effect can be explained by assuming that light:
(a) is a form of transverse waves
(b) is a form of longitudinal waves
(c) can be polarised
(d) consists of quanta

198. The photoelectric effect supports quantum nature of light because:
(a) there is a minimum frequency of light below which no photoelectrons are emitted
(b) the maximum kinetic energy of photoelectrons depends only on the frequency of light and not on its intensity
(c) even when metal surface is faintly illuminated the photoelectrons leave the surface immediately
(d) electric charge of photoelectrons is quantised

199. The mass of a proton at rest is: **(CBSE 1991)**
(a) zero (b) 1.67×10^{-35} kg
(c) one amu (d) 9×10^{-31} kg

200. Momentum of a photon of wavelength λ is: **(CBSE 1993)**
(a) h/λ (b) zero (c) $h\lambda/c^2$ (d) $h\lambda/c$

201. When X-rays pass through air they:
(a) produce light track in the air
(b) ionise the gas

(c) produce fumes in the air
(d) accelerate gas atoms

202. X-rays: **(CPMT 1991)**
(a) are deflected in a magnetic field
(b) are deflected in an electric field
(c) remain undeflected by both the fields
(d) are deflected in both the fields

203. Find the frequency of light that corresponds to photons of energy 5.0×10^{-5} erg: **(AIIMS 2010)**
(a) 7.5×10^{-21} sec^{-1} (b) 7.5×10^{-21} sec
(c) 7.5×10^{21} sec^{-1} (d) 7.5×10^{21} sec

[**Hint :** $\nu = \frac{E}{h} = \frac{5 \times 10^{-5} \text{ erg}}{6.63 \times 10^{-27} \text{ erg sec}}$
$= 7.54 \times 10^{21}$ sec^{-1}]

204. The energy of an electron in the first Bohr orbit of H-atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is/are: **(IIT 1998)**
(a) -3.4 eV (b) -4.2 eV
(c) -6.8 eV (d) $+6.8$ eV

205. The electrons identified by quantum numbers n and l, (i) $n = 4$, $l = 1$ (ii) $n = 4, l = 0$ (iii) $n = 3, l = 2$ (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest as: **(IIT 1999)**
(a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)

206. The wavelength of the radiation emitted when an electron falls from Bohr orbit 4 to 2 in hydrogen atom is: **(IIT 1999)**
(a) 243 nm (b) 972 nm
(c) 486 nm (d) 182 nm

207. The energy of the electron in the first orbit of He^+ is -871.6×10^{-20} J. The energy of the electron in the first orbit of hydrogen would be: **(IIT 1998)**
(a) -871.6×10^{-20} J (b) -435×10^{-20} J
(c) -217.9×10^{-20} J (d) -108.9×10^{-20} J

208. The wavelength associated with a golf ball weighing 200 g and moving with a speed of 5 m/h is of the order of: **(IIT 2000)**
(a) 10^{-10} m (b) 10^{-20} m (c) 10^{-30} m (d) 10^{-40} m

209. Who modified Bohr theory by introducing elliptical orbits for electron path? **(CBSE 1999)**
(a) Hund (b) Thomson
(c) Rutherford (d) Sommerfeld

210. The uncertainty in momentum of an electron is 1×10^{-5} kg ms^{-1}. The uncertainty in its position will be:
($h = 6.62 \times 10^{-34}$ kg-m^2-s) **(CBSE 1999; BHU 2010)**
(a) 1.05×10^{-28} m (b) 1.05×10^{-26} m
(c) 5.27×10^{-30} m (d) 5.25×10^{-28} m

211. The Bohr orbit radius for the hydrogen atom ($n = 1$) is approximately 0.530 Å. The radius for the first excited state ($n = 2$) orbits is: **(CBSE 1998)**
(a) 0.13 Å (b) 1.06 Å (c) 4.77 Å (d) 2.12 Å

212. The number of nodal planes in p_x-orbital is: **(IIT 2000)**
(a) one (b) two (c) three (d) zero

213. The angular momentum (L) of an electron in a Bohr orbit is given as: **(IIT 1997)**
(a) $L = \frac{nh}{2\pi}$ (b) $L = \sqrt{l(l+1)}\frac{h}{2\pi}$
(c) $L = \frac{mg}{2\pi}$ (d) $L = \frac{h}{4\pi}$

214. Ground state electronic configuration of nitrogen atom can be represented by: **(IIT 1999)**
1. $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow \mid \uparrow \mid \uparrow}$ 2. $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow \mid \downarrow \mid \uparrow}$
3. $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow \mid \downarrow \mid \downarrow}$ 4. $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\downarrow \mid \downarrow \mid \downarrow}$
(a) 1 only (b) 1,2 only (c) 1,4 only (d) 2,3 only

215. Which of the following statement(s) are correct?
1. Electronic configuration of Cr is [Ar] $3d^5 4s^1$ (At. No. of Cr = 24)
2. The magnetic quantum number may have negative value
3. In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (At. No. of Ag = 47)
4. The oxidation state of nitrogen in HN_3 is -3 **(IIT 1998)**
(a) 1,2,3 (b) 2,3,4 (c) 3,4 (d) 1,2,4

216. The electronic configuration of an element is $1s^2 2s^2 2p^6, 3s^2 3p^6\ 3d^5, 4s^1$. This represents: **(IIT 2000)**
(a) excited state (b) ground state
(c) cationic state (d) anionic state

217. The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for the electron spin represents: **(IIT 2000)**
(a) rotation of the electron in clockwise and anticlockwise directions respectively
(b) rotation of the electron in anticlockwise and clockwise directions respectively
(c) magnetic moment of electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogues

218. Rutherford's experiment, which established the nuclear model of the atom, used a beam of: **(IIT 2002)**
(a) β-particles, which impinged on a metal foil and got absorbed
(b) γ-rays, which impinged on a metal foil and ejected electrons
(c) helium atoms, which impinged on a metal foil and got scattered
(d) helium nuclei, which impinged on a metal foil and got scattered

219. How many moles of electrons weigh one kilogram?
(Mass of electron = 9.108×10^{-31} kg, Avogadro's number = 6.023×10^{23}) **(IIT 2002)**
(a) 6.023×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$
(c) $\frac{6.023}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.023} \times 10^{8}$

220. If the electronic configuration of nitrogen had $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$ because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates: **(IIT 2002)**

(a) Heisenberg uncertainty principle
(b) Hund's rule
(c) Pauli's exclusion principle
(d) Bohr postulates of stationary orbits

221. The orbital angular momentum of an electron in 2s-orbital is: [IIT 1996; AIEEE 2003; PMT (MP) 2004]

(a) $+\frac{1}{2}\frac{h}{2\pi}$ (b) zero
(c) $\frac{h}{2\pi}$ (d) $\sqrt{2}\,\frac{h}{2\pi}$

222. Calculate the wavelength (in nanometre) associated with a proton moving at 1×10^3 m sec^{-1}.
(mass of proton = 1.67×10^{-27} kg, $h = 6.63\times10^{-34}$ J sec) (AIEEE 2009)

(a) 0.032 nm (b) 0.40 nm
(c) 2.5 nm (d) 14 nm

[**Hint :** $\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}}{1.67\times10^{-27}\times10^3}$
$= 0.397\times10^{-9}$ m $= 0.4$ nm]

223. The value of Planck's constant is 6.63×10^{-34} J-s. The velocity of light is 3×10^8 m/sec. Which value is closest to the wavelength in nanometer of a quantum of light with frequency of 8×10^{15} sec^{-1}? [CBSE (PMT) 2003]

(a) 5×10^{-18} (b) 4×10^1
(c) 3×10^7 (d) 2×10^{-25}

224. Which of the following statements in relation to the hydrogen atom is correct? (AIEEE 2005)

(a) 3s-orbital is lower in energy than 3p-orbital
(b) 3p-orbital is lower in energy than 3d-orbital
(c) 3s-and 3p-orbitals are of lower energy than 3d-orbital
(d) 3s, 3p-and 3d-orbitals all have the same energy

225. The number of d-electrons in Ni (At. No. = 28) is equal to that of the: [CPMT (UP) 2004]

(a) s and p-electrons in F^-
(b) p-electrons in Ar (At. No. = 18)
(c) d-electrons in Ni^{2+}
(d) total number of electrons in N (At. No. = 7)

226. The number of radial nodes of 3s- and 2p-orbitals are respectively: [IIT (Screening) 2005]

(a) 2, 0 (b) 0, 2 (c) 1, 2 (d) 2, 1

227. Which of the following is not permissible? (DCE 2005)

(a) $n = 4, l = 3, m = 0$ (b) $n = 4, l = 2, m = 1$
(c) $n = 4, l = 4, m = 1$ (d) $n = 4, l = 0, m = 0$

228. According to Bohr theory, the angular momentum of electron in 5th orbit is: (AIEEE 2006)

(a) $25\frac{h}{\pi}$ (b) $1\frac{h}{\pi}$ (c) $10\frac{h}{\pi}$ (d) $2.5\frac{h}{\pi}$

229. Which of the following sets of quantum numbers represents the highest energy of an atom? (AIEEE 2007)

(a) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$
(b) $n = 3, l = 1, m = 1, s = +\frac{1}{2}$
(c) $n = 3, l = 2, m = 1, s = +\frac{1}{2}$
(d) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

230. In ground state, the radius of hydrogen atom is 0.53 Å. The radius of Li^{2+} ion ($Z = 3$) in the same state is: [PET (Raj.) 2007]

(a) 0.17 Å (b) 1.06 Å (c) 0.53 Å (d) 0.265 Å

231. How many d-electrons in Cu^+ (At. No. = 29) can have the spin quantum number $(-\frac{1}{2})$? (SCRA 2007)

(a) 3 (b) 7 (c) 5 (d) 9

232. Which of the following electronic configurations, an atom has the lowest ionisation enthalpy? [CBSE (Med.) 2007]

(a) $1s^2 2s^2 2p^3$ (b) $1s^2 2s^2 2p^6 3s^1$
(c) $1s^2 2s^2 2p^6$ (d) $1s^2 2s^2 2p^5$

233. The measurement of the electron position is associated with an uncertainty in momentum, which is equal to 1×10^{-18} g cm s^{-1}. The uncertainty in electron velocity is: (mass of an electron is 9×10^{-28} g) [CBSE-PMT (Pre.) 2008]

(a) 1×10^5 cm s^{-1} (b) 1×10^{11} cm s^{-1}
(c) 1×10^9 cm s^{-1} (d) 1×10^6 cm s^{-1}

234. The ionization enthalpy of hydrogen atom is 1.312×10^6 J mol^{-1}. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ is : (AIEEE 2008)

(a) 9.84×10^5 J mol^{-1} (b) 8.51×10^5 J mol^{-1}
(c) 6.56×10^5 J mol^{-1} (d) 7.56×10^5 J mol^{-1}

[**Hint :** $E_1 = -1.312\times10^6$ J mol^{-1}

$$E_2 = \frac{E_1}{2^2} = -\frac{1.312\times10^6}{4}\ \text{J mol}^{-1}$$

$$\Delta E = (E_2 - E_1) = 1.312\times10^6\left(1-\frac{1}{4}\right)$$

$$= \frac{3}{4}\times1.312\times10^6 = 9.84\times10^5\ \text{J mol}^{-1}]$$

235. The wavelengths of electron waves in two orbits is 3 : 5. The ratio of kinetic energy of electrons will be: (EAMCET 2009)

(a) 25 : 9 (b) 5 : 3
(c) 9 : 25 (d) 3 : 5

[**Hint :** We know, $\lambda = \frac{h}{\sqrt{2Em}}$

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{E_2}{E_1}}$$

$$\frac{3}{5} = \sqrt{\frac{E_2}{E_1}}$$

$\therefore$ $E_1 : E_2 = 25 : 9$]

236. Electrons with a kinetic energy of 6.023×10^4 J/mol are evolved from the surface of a metal, when it is exposed to radiation of wavelength of 600 nm. The minimum amount of energy required to remove an electron from the metal atom is : (EAMCET 2009)

(a) 2.3125×10^{-19} J (b) 3×10^{-19} J
(c) 6.02×10^{-19} J (d) 6.62×10^{-34} J

[**Hint :** Absorbed energy = Threshold energy + kinetic energy of photoelectron

$$\frac{hc}{\lambda} = E_0 + KE$$

$$\frac{6.62\times10^{-34}\times3\times10^8}{600\times10^{-9}} = E_0 + \frac{6.023\times10^4}{6.023\times10^{23}}\ \text{J/atom}$$

$$3.31\times10^{-19} = E_0 + 1\times10^{-19}$$
$$E_0 = 2.31\times10^{-19}\text{ J}]$$

237. For the Paschen series the value of n_1 and n_2 in the expression $\Delta E = R_H \times c\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ is: **[JEE (WB) 2009]**

(a) $n_1 = 1, n_2 = 2, 3, 4 \ldots$
(b) $n_1 = 2, n_2 = 3, 4, 5 \ldots$
(c) $n_1 = 3, n_2 = 4, 5, 6 \ldots$
(d) $n_1 = 4, n_2 = 5, 6, 7 \ldots$

238. Ionization energy of He^+ is 19.6×10^{-18} J atom^{-1}. The energy of the first stationary state ($n = 1$) of Li^{2+} is: **(AIEEE 2010)**

(a) -2.2×10^{-15} J atom^{-1} (b) 8.82×10^{-17} J atom^{-1}
(c) 4.41×10^{-16} J atom^{-1} (d) -4.41×10^{-17} J atom^{-1}

[**Hint:** $\frac{I_{He^+}}{I_{Li^{2+}}} = \frac{Z_1^2}{Z_2^2}$

$$\frac{19.6\times10^{-18}}{I_{Li^{2+}}} = \frac{4}{9}$$
$$I_{Li^{2+}} = \frac{9}{4}\times19.6\times10^{-18}$$
$$= 44.1\times10^{-18}$$
$$= 4.41\times10^{-17}\text{ J atom}^{-1}$$
$$E_{Li^{2+}} = -4.41\times10^{-17}\text{ J atom}^{-1}]$$

239. The energy required to break one mole of Cl—Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking single Cl—Cl bond is: **(AIEEE 2010)**
($c = 3\times10^8$ m sec^{-1}, $N_A = 6.023\times10^{23}$ mol^{-1})

(a) 700 nm (b) 494 nm (c) 594 nm (d) 640 nm

[**Hint:** Bond energy of single bond $= \frac{242}{6.023\times10^{23}}$
$$= 4.017\times10^{-22}\text{ kJ}$$
$$= 4.017\times10^{-19}\text{ J}$$
$$E = \frac{hc}{\lambda}$$
$$4.017\times10^{-19} = \frac{6.626\times10^{-34}\times3\times10^8}{\lambda}$$
$$\lambda = 4.94\times10^{-7}\text{ m} = 494\text{ nm}]$$

240. In Sommerfeld's modification of Bohr's theory, the trajectory of an electron in a hydrogen atom is: **[JEE (WB) 2010]**

(a) perfect ellipse
(b) a closed ellipse like curve, narrower at the perihelion position and flatter at the aphelion position
(c) a closed loop on spherical surface
(d) a rosette

Set-2: The questions given below may have more than one correct answers

1. Correct order of radius of the 1st orbit of H, He^+, Li^{2+} and Be^{3+} is:

(a) H $> He^+ > Li^{2+} > Be^{3+}$
(b) $Be^{3+} > Li^{2+} > He^+ >$ H
(c) $He^+ > Be^{3+} > Li^{2+} >$ H
(d) $He^+ >$ H $> Li^{2+} > Be^{3+}$

2. Which is the correct relationship?

(a) E_1 of H = 1/2 E_2 of He^+ = 1/3 E_3 of Li^{2+} = 1/4 E_4 of Be^{3+}
(b) $E_1(H) = E_2(He^+) = E_3(Li^{2+}) = E_4(Be^{3+})$
(c) $E_1(H) = 2E_2(He^+) = 3E_3(Li^{2+}) = 4E_4(Be^{3+})$
(d) No relation

3. Which is correct for any kind of species?

(a) $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$
(b) $(E_2 - E_1) < (E_3 - E_2) < (E_4 - E_3)$
(c) $(E_2 - E_1) = (E_3 - E_2) = (E_4 - E_3)$
(d) $(E_2 - E_1) = 1/4(E_3 - E_2) = 1/9(E_4 - E_3)$

4. No. of visible lines when an electron returns from 5th orbit to ground state in H spectrum is:

(a) 5 (b) 4 (c) 3 (d) 10

5. Quantum numbers $l = 2$ and $m = 0$ represent which orbital?

(a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{z^2} (d) d_{zx}

6. If n and l are principal and azimuthal quantum numbers respectively, then the expression for calculating the total numbers of electrons in any energy level is:

(a) $\sum_{l=0}^{l=n} 2(2l+1)$ (b) $\sum_{l=1}^{l=n-1} 2(2l+1)$
(c) $\sum_{l=0}^{l=n+1} 2(2l+1)$ (d) $\sum_{l=0}^{l=n-1} 2(2l+1)$

7. Order of no. of revolution/sec $\gamma_1, \gamma_2, \gamma_3$ and γ_4 for I, II, III and IV orbits is:

(a) $\gamma_1 > \gamma_2 > \gamma_3 > \gamma_4$ (b) $\gamma_4 > \gamma_3 > \gamma_2 > \gamma_1$
(c) $\gamma_1 > \gamma_2 > \gamma_4 > \gamma_3$ (d) $\gamma_2 > \gamma_3 > \gamma_4 > \gamma_1$

8. Consider the following statements:

(A) Electron density in the xy-plane in $3d_{x^2-y^2}$ orbital is zero
(B) Electron density in the xy-plane in $3d_{z^2}$ orbital is zero
(C) $2s$-orbital has one nodal surface
(D) For $2p_z$-orbital yz is the nodal plane,

Which are the correct statements?

(a) (A) and (C) (b) (B) and (C)
(c) Only (B) (d) (A), (B), (C) and (D)

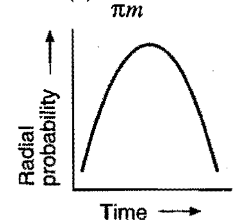
9. The first emission line in the H-atom spectrum in the Balmer series appears at:

(a) $\frac{5R}{36}$ cm^{-1} (b) $\frac{3R}{4}$ cm^{-1} (c) $\frac{7R}{144}$ cm^{-1} (d) $\frac{9R}{400}$ m^{-1}

10. 1 BM is equal to:

(a) $\frac{hc}{m\pi e^4}$ (b) $\frac{hc}{4\pi m}$ (c) $\frac{e^2hc}{4m}$ (d) $\frac{ehc}{\pi m}$

11. Radial probability distribution curve is shown for s-orbital. The curve is:



(a) $1s$
(b) $2s$
(c) $3s$
(d) $4s$

12. dz^2 orbital has:

(a) a lobe along z-axis and a ring along xy-plane
(b) a lobe along z-axis and a lobe along xy-plane
(c) a lobe along z-axis and a ring along yz-plane
(d) a lobe and ring along z-axis

13. When a light of frequency ν_1 is incident on a metal surface the photoelectrons emitted have twice the kinetic energy as did the photoelectron emitted when the same metal has irradiated with light of frequency ν_2. What will be the value of threshold frequency?
(a) $\nu_0 = \nu_1 - \nu_2$ (b) $\nu_0 = \nu_1 - 2\nu_2$
(c) $\nu_0 = 2\nu_1 - \nu_2$ (d) $\nu_0 = \nu_1 + \nu_2$

14. Heisenberg's uncertainty principle is not valid for:
(a) moving electrons (b) motor car
(c) stationary particles (d) all of these

15. Consider these electronic configurations for neutral atoms;
(i) $1s^2 2s^2 2p^6 3s^1$ (ii) $1s^2 2s^2 2p^6 4s^1$
Which of the following statements is/are false?
(a) Energy is required to change (i) to (ii)
(b) (i) represents 'Na' atom
(c) (i) and (ii) represent different elements
(d) More energy is required to remove one electron from (i) than (ii)

16. For the energy levels in an atom which one of the following statements is/are correct?
(a) There are seven principal electron energy levels
(b) The second principal energy level can have 4 subenergy levels and contain a maximum of 8 electrons
(c) The M energy level can have a maximum of 32 electrons
(d) The $4s$ subenergy level is at a lower energy than the $3d$ subenergy level

17. Which of the following statements are correct for an electron that has $n = 4$ and $m = -2$?
(a) The electron may be in a d-orbital
(b) The electron is in the fourth principal electronic shell
(c) The electron may be in a p-orbital
(d) The electron must have the spin quantum number $= +1/2$

18. The angular momentum of electron can have the value(s):
(a) $\frac{h}{2\pi}$ (b) $\frac{h}{\pi}$
(c) $\frac{2h}{\pi}$ (d) $\frac{5}{2}\frac{h}{2\pi}$

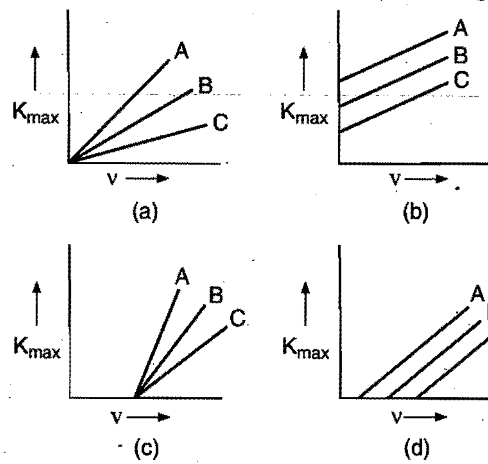
19. Which of the following statements is/are wrong?
(a) If the value of $l = 0$, the electron distribution is spherical
(b) The shape of the orbital is given by magnetic quantum no.
(c) Angular moment of 1s, 2s, 3s electrons are equal
(d) In an atom, all electrons travel with the same velocity

20. Consider the following sets of quantum numbers:

	n	l	m	s
(A)	3	0	0	$+\frac{1}{2}$
(B)	2	2	1	$+\frac{1}{2}$
(C)	4	3	-2	$-\frac{1}{2}$
(D)	1	0	-1	$-\frac{1}{2}$
(E)	3	2	3	$+\frac{1}{2}$

Which of the following sets of quantum numbers is not possible? **[CBSE (Med.) 2007]**
(a) (A), (B), (C) and (D) (b) (B), (D) and (E)
(c) (A) and (C) (d) (B), (C) and (D)

21. For three different metals A, B, C photo-emission is observed one by one. The graph of maximum kinetic energy versus frequency of incident radiation are sketched as : **[BHU (Screening) 2010]**



22. For which of the following species, the expression for the energy of electron in the n^{th} $\left[E_n = -\frac{13.6 Z^2}{n^2} \text{eV atom}^{-1}\right]$ has the validity? **[BHU (Mains) 2010]**
(a) Tritium (b) Li^{2+}
(c) Deuterium (d) He^{2+}

Assertion-Reason TYPE QUESTIONS

Set–1

The questions given below consist of an **'Assertion' (A)** and the **'Reason' (R).** Use the following keys for the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct reason for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) F-atom has less electron affinity than Cl^- atom.
(R) Additional electrons are repelled more effectively by $3p$ electrons in Cl atom than by $2p$ electrons in F-atom.

2. (A) Nuclide $^{30}_{13}Al$ is less stable than $^{40}_{20}Ca$.
(R) Nuclide having odd number of protons and neutrons are generally unstable. **(IIT 1998)**

3. (A) The first IE of Be is greater than that of B.
(R) $2p$-orbital is lower in energy than $2s$.

4. (A) The electronic configuration of nitrogen atom is represented as:

⇅		⇅		↑	↑	↑

and not as:

⇅		⇅		⇅	↑	

(R) The electronic configuration of the ground state of an atom is the one which has the greatest multiplicity.

5. (A) The atomic radii of the elements of oxygen family are smaller than the atomic radii of corresponding elements of the nitrogen family.
(R) The members of oxygen family are all more electronegative and thus have lower value of nuclear charge than those of the nitrogen family.

6. (A) For $n = 3$, l may be 0, 1 and 2 and may be 0, ±1 and 0, ±1 and ±2.
(R) For each value of n, there are 0 to $(n - 1)$ possible values of l; for each value of l, there are 0 to $\pm l$ values of m.

7. (A) An orbital cannot have more than two electrons.
(R) The two electrons in an orbital create opposite magnetic field.

8. (A) The configuration of B-atom cannot be $1s^2 2s^2$.
(R) Hund's rule demands that the configuration should display maximum multiplicity.

9. (A) The ionization energy of N is more than that of O.
(R) Electronic configuration of N is more stable due to half-filled $2p$-orbitals.

10. (A) p-orbital is dumb-bell shaped.
(R) Electron present in p-orbital can have any one of the three values of magnetic quantum number, *i.e.*, 0, +1 or −1.

Set–2

The questions given below consist of two statements as **'Assertion' (A)** and **'Reason' (R);** while answering these choose any one of them:

(a) If (A) and (R) are both correct and (R) is the correct reason for (A).
(b) If (A) and (R) are both correct but (R) is not the correct reason for (A).
(c) If (A) is true but (R) is false.
(d) If both (A) and (R) are false.

11. (A) A special line will be seen for $2p_x - 2p_y$ transition.
(R) Energy is released in the form of wave of light when the electron drops from $2p_x$ to $-2p_y$ orbital. **(AIIMS 1996)**

12. (A) Ionization potential of Be (At. No. = 4) is less than B (At. No. = 5).
(R) The first electron released from Be is of p-orbital but that from B is of s-orbital. **(AIIMS 1997)**

13. (A) In Rutherford's gold foil experiment, very few α-particles are deflected back.
(R) Nucleus present inside the atom is heavy.

14. (A) Limiting line in the Balmer series has a wavelength of 364.4 mm.
(R) Limiting line is obtained for a jump of electron from $n = \infty$.

15. (A) Each electron in an atom has two spin quantum numbers.
(R) Spin quantum numbers are obtained by solving Schrödinger wave equation.

16. (A) There are two spherical nodes in $3s$-orbital.
(R) There is no planar node in $3s$-orbital.

17. (A) In an atom, the velocity of electron in the higher orbits keeps on decreasing.
(R) Velocity of electrons is inversely proportional to radius of the orbit.

18. (A) If the potential difference applied to an electron is made 4 times, the de Broglie wavelength associated is halved.
(R) On making potential difference 4 times, velocity is doubled and hence d is halved.

19. (A) Angular momentum of $1s$, $2s$, $3s$, etc., all have spherical shape.
(R) $1s$, $2s$, $3s$, etc., all have spherical shape.

20. (A) The radial probability of $1s$ electron first increases, till it is maximum at 53 Å and then decreases to zero.
(R) Bohr radius for the first orbit is 53 Å.

21. (A) On increasing the intensity of incident radiation, the number of photoelectrons ejected and their KE increases.
(R) Greater the intensity means greater the energy which in turn means greater the frequency of the radiation.

22. (A) A spectral line will be seen for a $2p_x - 2p_y$ transition.
(R) Energy is released in the form of wave of light when the electron drops from $2p_x$ to $2p_y$ orbital. **(VMMC 2007)**

Answers : OBJECTIVE QUESTIONS

- **Set–1**

1. (b)	2. (a)	3. (c)	4. (d)	5. (c)	6. (b)	7. (d)	8. (a)
9. (a)	10. (b)	11. (d)	12. (d)	13. (a)	14. (c)	15. (b)	16. (a)
17. (c)	18. (d)	19. (b)	20. (c)	21. (d)	22. (c)	23. (b)	24. (a)
25. (d)	26. (b)	27. (d)	28. (a)	29. (d)	30. (b)	31. (c)	32. (b)
33. (a)	34. (c)	35. (d)	36. (a)	37. (c)	38. (a)	39. (b)	40. (c)
41. (c)	42. (b)	43. (d)	44. (d)	45. (c)	46. (a)	47. (b)	48. (d)
49. (d)	50. (c)	51. (b)	52. (b)	53. (a)	54. (b)	55. (a)	56. (a)
57. (c)	58. (d)	59. (a)	60. (d)	61. (c)	62. (a)	63. (a)	64. (b)
65. (a)	66. (d)	67. (d)	68. (b)	69. (c)	70. (c)	71. (a)	72. (d)
73. (d)	74. (b)	75. (c)	76. (d)	77. (b)	78. (d)	79. (a)	80. (d)
81. (b)	82. (b)	83. (c)	84. (a)	85. (b)	86. (a)	87. (b)	88. (c)
89. (b)	90. (d)	91. (a)	92. (d)	93. (a)	94. (a)	95. (b)	96. (c)
97. (a)	98. (d)	99. (b)	100. (b)	101. (d)	102. (d)	103. (a)	104. (c)
105. (c)	106. (c)	107. (d)	108. (b)	109. (d)	110. (a)	111. (a)	112. (b)
113. (c)	114. (d)	115. (a)	116. (d)	117. (b)	118. (a)	119. (c)	120. (c)
121. (d)	122. (b)	123. (d)	124. (c)	125. (a)	126. (a)	127. (c)	128. (c)
129. (b)	130. (b)	131. (c)	132. (c)	133. (c)	134. (b)	135. (c)	136. (d)
137. (b)	138. (a)	139. (a)	140. (a)	141. (b)	142. (c)	143. (c)	144. (a)
145. (b)	146. (c)	147. (d)	148. (c)	149. (d)	150. (d)	151. (a)	152. (d)
153. (c)	154. (a)	155. (c)	156. (a)	157. (a)	158. (c)	159. (c)	160. (d)
161. (c)	162. (c)	163. (b)	164. (b)	165. (a)	166. (b)	167. (b)	168. (b)
169. (d)	170. (d)	171. (b)	172. (b)	173. (d)	174. (b)	175. (c)	176. (a)
177. (d)	178. (b)	179. (d)	180. (a)	181. (d)	182. (a)	183. (a, b)	184. (c)
185. (a)	186. (a)	187. (b)	188. (b)	189. (b)	190. (b)	191. (a)	192. (c)
193. (c)	194. (b)	195. (a)	196. (a)	197. (d)	198. (a)	199. (c)	200. (a)
201. (a)	202. (c)	203. (c)	204. (a)	205. (a)	206. (b)	207. (c)	208. (c)
209. (d)	210. (c)	211. (d)	212. (a)	213. (a)	214. (c)	215. (a)	216. (b)
217. (d)	218. (d)	219. (d)	220. (c)	221. (b)	222. (b)	223. (b)	224. (d)
225. (c)	226. (a)	227. (c)	228. (d)	229. (c)	230. (a)	231. (c)	232. (b)
233. (c)	234. (a)	235. (a)	236. (a)	237. (c)	238. (d)	239. (b)	240. (c)

- **Set–2**

1. (a)	2. (b)	3. (a)	4. (c)	5. (c)	6. (d)	7. (a)	8. (a)
9. (a)	10. (a)	11. (a)	12. (a)	13. (c)	14. (b, c)	15. (c, d)	16. (a, d)
17. (b, c)	18. (a, b, c)	19. (c)	20. (b)	21. (d)	22. (a, b, c)		

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (c)	2. (a)	3. (c)	4. (a)	5. (c)	6. (a)	7. (b)	8. (c)
9. (c)	10. (a)	11. (d)	12. (d)	13. (b)	14. (a)	15. (d)	16. (b)
17. (c)	18. (a)	19. (b)	20. (b)	21. (d)	22. (d)		

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain a single correct option:

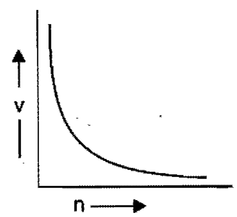
1. The configuration of Cr atom is $3d^5 4s^1$ but not $3d^4 4s^2$ due to reason R_1 and the configuration of Cu atom is $3d^{10} 4s^1$ but not $3d^9 4s^2$ due to reason R_2, R_1 and R_2 are:
   (a) R_1: The exchange energy of $3d^5 4s^1$ is greater than that of $3d^4 4s^2$.
   R_2: The exchange energy of $3d^{10} 4s^1$ is greater than that of $3d^9 4s^2$.
   (b) R_1: $3d^5 4s^1$ and $3d^4 4s^2$ have same exchange energy but $3d^5 4s^1$ is spherically symmetrical.
   R_2: $3d^{10} 4s^1$ is also spherically symmetrical.
   (c) R_1: $3d^5 4s^1$ has greater exchange energy than $3d^4 4s^2$.
   R_2: $3d^{10} 4s^1$ has spherical symmetry.
   (d) R_1: $3d^5 4s^1$ has greater energy than $3d^4 4s^2$.
   R_2: $3d^{10} 4s^1$ has greater energy than $3d^9 4s^2$.
   [**Hint:** $3d^5 4s^1$ is correct because it has greater exchange possibilities of unpaired electrons.

1	1	1	1	1
1	2	3	4	5

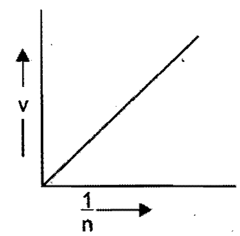
Exchange possibilities: (10) 1–2, 1–3, 1–4, 1–5; 2–3, 2–4, 2–5; 3–4, 3–5; 4–5

$3d^{10} 4s^1$ is correct because $3d^{10}$-orbitals are spherically symmetrical.]

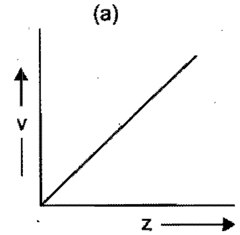
2. Which of the following graphs is incorrect ?



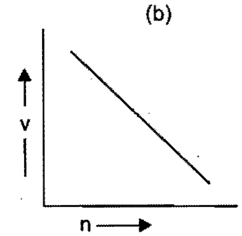
(a)



(b)



(c)



(d)

3. Which among the following is correct of ${}_5B$ in normal state?

	2s	2p			
(a)	↑↑		↑		: Against Hund's rule
(b)	↑	↑	↑		: Against aufbau principle as well as Hund's rule
(c)	↑↑	↑			: Violation of Pauli's exclusion principle and not Hund's rule
(d)	↑↓	↑			: Against aufbau principle

4. Maximum value $(n + l + m)$ for unpaired electrons in second excited state of chlorine ${}_{17}Cl$ is:
   (a) 28 (b) 25
   (c) 20 (d) none of these
   [**Hint:** Configuration in second excited state may be given as:

	3p			3d				
	1	1	1	1	1			
n	3	3	3	3	3			
l	1	1	1	2	2			
m	−1	0	+1	+2	+1			

Total $n + l + m = 25$]

5. Which of the following is correctly matched?
   (a) Momentum of H-atom when electrons return from $n = 2$ to $n = 1$: $\frac{3Rh}{4}$
   (b) Momentum of photon : Independent of wavelength of light
   (c) e/m ratio of anode rays : Independent of gas in the discharge tube
   (d) Radius of nucleus : $(\text{Mass no.})^{1/2}$
   [**Hint:**
   $$\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3R}{4}$$
   $$\lambda = \frac{h}{p}$$
   $$p = \frac{h}{\lambda} = h \times \frac{3R}{4} = \frac{3Rh}{4}$$]

6. In hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electrons from Bohr orbit of hydrogen?
   (a) $4 \rightarrow 1$ (b) $2 \rightarrow 5$ (c) $3 \rightarrow 2$ (d) $5 \rightarrow 2$

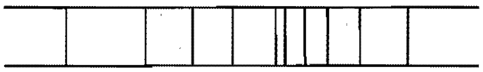
7. In which of the following pairs is the probability of finding the electron in xy-plane zero for both orbitals?
   (a) $3d_{yz}, 4d_{x^2-y^2}$ (b) $2p_z, d_{z^2}$
   (c) $4d_{zx}, 3p_z$ (d) None of these

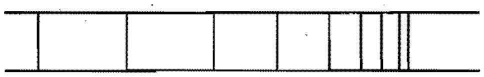
8. In which of the following orbital diagrams are both Pauli's exclusion principle and Hund's rule violated?
   (a) [↑↓] [↑ | ↑↓ | ↑] (b) [↑↓] [↑ | ↑↓ |]
   (c) [↑↓] [↑↓ | ↑↑ | ↓] (d) [↓↓] [↑↓ | ↑ |]

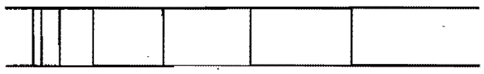
9. The distance between 3rd and 2nd Bohr orbits of hydrogen atom is:
   (a) 0.529×10^{-8} cm (b) 2.645×10^{-8} cm
   (c) 2.116×10^{-8} cm (d) 1.058×10^{-8} cm
   [**Hint:** $r_3 - r_2 = (3^2 - 2^2) \times 0.529 \times 10^{-8}$ cm]

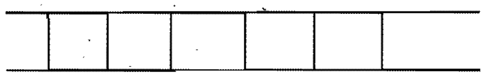
10. Which diagram represents the best appearance of the line spectrum of atomic hydrogen in the visible region?
    [PET (Kerala) 2007]

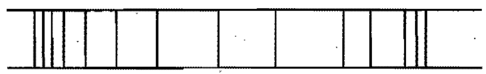
Increasing wavelength

(a) 

(b) 

(c) 

(d) 

(e) 

11. The 'm' value for an electron in an atom is equal to the number of m values for $l = 1$. The electron may be present in:
(a) $3d_{x^2-y^2}$ (b) $5f_{x(x^2-y^2)}$
(c) $4f_{x^3/z}$ (d) none of these
[**Hint**: Total values of $m = (2l + 1) = 3$ for $l = 1$
$m = 3$ is for f-subshell orbitals.]

12. If m = magnetic quantum number, l = azimuthal quantum number, then:
(a) $m = l + 2$ (b) $m = 2l^2 + 1$
(c) $l = \frac{m-1}{2}$ (d) $l = 2m + 1$
[**Hint:** Magnetic quantum number 'm' lies between $(-l, 0, +l)$; thus total possible values of 'm' will be $(2l + 1)$.
$m = 2l + 1$, *i.e.*, $l = \frac{m-1}{2}$]

13. What are the values of the orbital angular momentum of an electron in the orbitals 1s, 3s, 3d and 2p?
(a) $0, 0, \sqrt{6}\,\hbar, \sqrt{2}\,\hbar$ (b) $1, 1, \sqrt{4}\,\hbar, \sqrt{2}\,\hbar$
(c) $0, 1, \sqrt{6}\,\hbar, \sqrt{3}\,\hbar$ (d) $0, 0, \sqrt{20}\,\hbar, \sqrt{6}\,\hbar$
[**Hint:** Orbital angular momentum $= \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{l(l+1)}\,\hbar$]

14. After np-orbitals are filled, the next orbital filled will be:
(a) $(n+1)s$ (b) $(n+2)p$ (c) $(n+1)d$ (d) $(n+2)s$

15. The ratio of $(E_2 - E_1)$ to $(E_4 - E_3)$ for the hydrogen atom is approximately equal to:
(a) 10 (b) 15 (c) 17 (d) 12
[**Hint:**
$$\frac{E_4 - E_3}{E_2 - E_1} = \frac{\left(-\frac{1}{16}\right) - \left(-\frac{1}{9}\right)}{\left(-\frac{1}{4}\right) - (-1)} = \frac{\frac{1}{9} - \frac{1}{16}}{\frac{3}{4}} = \frac{7}{144} \times \frac{4}{3} = \frac{7}{108} \approx \frac{1}{15}$$]

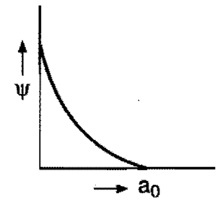
16. Which of the following electronic configurations has zero spin multiplicity?
(a) | ↑ | ↑ | ↑ | (b) | ↑ | ↑ | ↓ |
(c) | ↑ | ↓ | ↓ | (d) | ↓ | ↓ | ↓ |
[**Hint:** Spin multiplicity $= (2\Sigma s + 1)$]

17. A photosensitive material would emit electrons if excited by photons beyond a threshold. To overcome the threshold, one would increase: **(VITEEE 2007)**
(a) the voltage applied to the light source
(b) the intensity of light
(c) the wavelength of light
(d) the frequency of light

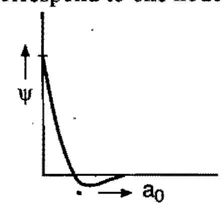
18. Which of the following electronic configurations have the highest exchange energy?

	3d					4s
(a)	↑	↑	↑			↑
(b)	↑	↑	↑	↑	↑	↑
(c)	↑↓	↑↓	↑↓	↑↓	↑	↑
(d)	↑↓	↑↓	↑↓	↑↓	↑↓	↑

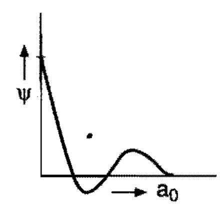
19. Which of the following graphs correspond to one node?



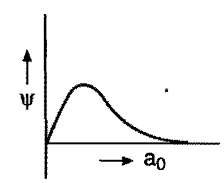
(a)



(b)



(c)



(d)

20. Angular distribution functions of all orbitals have:
(a) l nodal surfaces (b) $(l-1)$ nodal surfaces
(c) $(n+l)$ nodal surfaces (d) $(n-l-1)$ nodal surfaces

21. If uncertainty in position and momentum are equal then uncertainty in velocity is: **[CBSE-PMT (Pre.) 2008]**
(a) $\sqrt{\frac{h}{\pi}}$ (b) $\sqrt{\frac{h}{2\pi}}$ (c) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (d) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$
[**Hint:** $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$
$\Delta p \geq \sqrt{\frac{h}{4\pi}}$ when $\Delta x = \Delta p$
$m\Delta v \geq \sqrt{\frac{h}{4\pi}}$
$\Delta v \geq \frac{1}{2m}\sqrt{\frac{h}{\pi}}$]

22. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number 3 is:
(a) 3 (b) 4 (c) 2 (d) 1
[**Hint:** $m = 3, l = 3, n = 4$
For, $n = 4$, number of waves will be 4.]

23. The number of elliptical orbits excluding circular orbits in the N-shell of an atom is:
(a) 3 (b) 4 (c) 2 (d) 1
[**Hint:** For, N-shell, $n = 4$. This shell will have one circular and three elliptical orbits.]

24. From the electronic configuration of the given elements K, L, M and N, which one has the highest ionization potential?
(a) $M = [Ne]\, 3s^2 3p^2$ (b) $L = [Ne]\, 3s^2 3p^3$
(c) $K = [Ne]\, 3s^2 3p^1$ (d) $N = [Ar]\, 3d^{10}, 4s^2 4p^3$
[**Hint:** L has half-filled p-subshell and it is smaller than N, hence, L will have the highest ionization potential.]

25. Which of the following pairs of electrons is excluded from an atom?
(a) $n = 2, l = 0, m = 0, s = +\frac{1}{2}$ and $n = 2, l = 0, m = 0, s = +\frac{1}{2}$
(b) $n = 2, l = 1, m = +1, s = +\frac{1}{2}$ and $n = 2, l = 1, m = -1, s = +\frac{1}{2}$
(c) $n = 1, l = 0, m = 0, s = +\frac{1}{2}$ and $n = 1, l = 0, m = 0, s = -\frac{1}{2}$
(d) $n = 3, l = 2, m = -2, s = +\frac{1}{2}$ and $n = 3, l = 0, m = 0, s = +\frac{1}{2}$
[**Hint:** Both 2s electrons have same spin, hence excluded from the atom.]

26. Given set of quantum numbers for a multielectron atom is:

n	l	m	s
2	0	0	+1/2
2	0	0	−1/2

What is the next higher allowed set of 'n' and 'l' quantum numbers for this atom in the ground state?
(a) $n = 2, l = 0$ (b) $n = 2, l = 1$
(c) $n = 3, l = 0$ (d) $n = 3, l = 1$

27. In how many elements does the last electron have the quantum numbers of $n = 4$ and $l = 1$?
(a) 4 (b) 6 (c) 8 (d) 10
[**Hint:** $n = 4, l = 1$ represent $4p$-subshell containing six electrons. Thus, there will be six elements having $4p^1$ to $4p^6$ electronic configuration.]

28. If there are three possible values $(-1/2, 0, +1/2)$ for the spin quantum, then electronic configuration of K (19) will be:
(a) $1s^3, 2s^3 2p^9, 3s^3 3p^1$ (b) $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$
(c) $1s^2, 2s^2 2p^9, 3s^2 3p^4$ (d) none of these

29. If the radius of first Bohr orbit of hydrogen atom is 'x' then de Broglie wavelength of electron in 3rd orbit is nearly:
(a) $2\pi x$ (b) $6\pi x$ (c) $9x$ (d) $\frac{x}{3}$
[**Hint:** $r_n = n^2 r_1$

$$r_3 = 9r_1 = 9x$$
$$mvr = n\frac{h}{2\pi}$$
$$mv9x = 3\frac{h}{2\pi}$$
$$\frac{h}{mv} = 6\pi x$$
$$\lambda = 6\pi x]$$

30. How many times does light travel faster in vacuum than an electron in Bohr first orbit of hydrogen atom?
(a) 13.7 times (b) 67 times (c) 137 times (d) 97 times
[**Hint:**
$$v = \frac{Z}{n} \times 2.188 \times 10^8 \text{ cm/sec}$$
$$v_1 = \frac{1}{1} \times 2.188 \times 10^8 \text{ cm/sec}$$
$$\frac{\text{Velocity of light}}{\text{Velocity of electron}} = \frac{3 \times 10^{10}}{2.188 \times 10^8} = 137 \text{ times}]$$

31. A compound of vanadium has a magnetic moment of 1.73 BM. The electronic configuration of vanadium ion in the compound is:
(a) $[Ar]\, 3d^2$ (b) $[Ar] 3d^1 4s^0$ (c) $[Ar]\, 3d^3$ (d) $[Ar]\, 3d^0 4s^1$
[**Hint:** Magnetic moment $= \sqrt{n(n+2)}$ BM
$$1.73 = \sqrt{n(n+2)}$$
$$\sqrt{3} = \sqrt{n(n+2)}$$
$n = 1$ (number of unpaired electrons)
$V_{22} \rightarrow 3d^2 4s^2$
$V^{3+} \rightarrow 3d^1 4s^0$ (has one unpaired electron)]

32. The orbital angular momentum of an electron in p-orbital is: **[PET (Kerala) 2006]**
(a) zero (b) $\frac{h}{\sqrt{2}\pi}$ (c) $\frac{h}{2\pi}$ (d) $\frac{1}{2}\frac{h}{2\pi}$
(e) $\frac{h}{2\sqrt{2}\pi}$

33. When a hydrogen atom emits a photon of energy 12.1 eV, the orbital angular momentum changes by:
(a) 1.05×10^{-34} J sec (b) 2.11×10^{-34} J sec
(c) 3.16×10^{-34} J sec (d) 4.22×10^{-34} J sec
[**Hint:** Emission of photon of 12.1 eV corresponds to the transition from $n = 3$ to $n = 1$.
∴ Change in angular momentum
$$= (n_2 - n_1)\frac{h}{2\pi}$$
$$= (3-1)\frac{h}{2\pi} = \frac{h}{\pi}$$
$$= \frac{6.626 \times 10^{-34}}{3.14}$$
$$= 2.11 \times 10^{-34} \text{ J sec}]$$

34. The total energy of the electron of H-atom in the second quantum state is $-E_2$. The total energy of the He^+ atom in the third quantum state is:
(a) $-\left(\frac{3}{2}\right)E_2$ (b) $-\left(\frac{2}{3}\right)E_2$ (c) $-\left(\frac{4}{9}\right)E_2$ (d) $-\left(\frac{16}{9}\right)E_2$
[**Hint:** Energy of electrons in nth state
$$= -\frac{Z^2}{n^2} \times 13.6 \text{ eV}$$

$$E_2(\text{H}) = -\frac{13.6}{1}\text{ eV}$$

$$E_3(\text{He}^+) = -\frac{13.6 \times 4}{9}\text{ eV}$$

$$\frac{E_2}{E_3} = \frac{9}{4} \quad \text{or} \quad E_3 = \frac{4}{9}E_2$$

For negative value of E_2, E_3 will also be negative.]

35. What is the ratio of the Rydberg constant for helium to hydrogen atom?

(a) 1/2 (b) 1/4 (c) 1/8 (d) 1/16

[Hint: $R = \frac{-2\pi^2 mZ^2 e^4}{ch^3}$

$$\frac{R_{\text{He}}}{R_{\text{H}}} = \frac{2 \times 2^2}{1 \times 1^2} = 8$$

$\therefore$ $\frac{R_{\text{H}}}{R_{\text{He}}} = \frac{1}{8}$]

36. If the kinetic energy of a particle is doubled, de Broglie wavelength becomes:

(a) 2 times (b) 4 times (c) $\sqrt{2}$ times (d) $\frac{1}{\sqrt{2}}$ times

[Hint: $\lambda = \frac{h}{\sqrt{2Em}}$, where, E = Kinetic energy of the particle

$\therefore$ $\lambda_1 = \frac{h}{\sqrt{2Em}}$; $\lambda_2 = \frac{h}{\sqrt{2 \times 2Em}}$

$\therefore$ $\frac{\lambda_1}{\lambda_2} = \sqrt{2}$, *i.e.*, $\lambda_2 = \frac{\lambda_1}{\sqrt{2}}$]

37. Imagine an atom made up of a proton and a hypothetical particle of double the mass of the electron but having the same charge as the electron. Apply the Bohr's atomic model and consider all possible transitions of this hypothetical particle to the first excited level. The largest wavelength photon that will be emitted has wavelength λ (given in terms of the Rydberg constant R for the hydrogen atom) equal to:

(a) $\frac{9}{5R}$ (b) $\frac{36}{5R}$ (c) $\frac{18}{5R}$ (d) $\frac{4}{R}$

[Hint: Energy is related to mass:

$$E_n \propto m$$

The longest wavelength λ_{max} photon will correspond to the transition of particle from $n = 3$ to $n = 2$

$$\frac{1}{\lambda_{max}} = 2R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\lambda_{max} = \frac{18}{5R} \text{]}$$

38. What is ratio of time periods (T_1/T_2) in second orbit of hydrogen atom to third orbit of He^+ ion?

(a) $\frac{8}{27}$ (b) $\frac{32}{27}$ (c) $\frac{27}{32}$ (d) $\frac{27}{8}$

[Hint : $T \propto \frac{n^3}{Z^2}$

$$\frac{T_1}{T_2} = \frac{n_1^3 \times Z_2^2}{Z_1^2 \times n_2^3} = \frac{2^3 \times 2^2}{1^2 \times 3^3} = \frac{32}{27} \text{]}$$

39. The de Broglie wavelength of an electron accelerated by an electric field of V volt is given by :

(a) $\lambda = \frac{1.23}{\sqrt{m}}$ (b) $\lambda = \frac{1.23m}{\sqrt{h}}$ (c) $\frac{1.23}{\sqrt{V}}\,nm$ (d) $\lambda = \frac{1.23}{V}$

40. An excited electron of H-atoms emits of photon of wavelength λ and returns in the ground state, the principal quantum number of excited state is given by :

(a) $\sqrt{\lambda R(\lambda R - 1)}$ (b) $\sqrt{\frac{\lambda R}{(\lambda R - 1)}}$

(c) $\frac{1}{\sqrt{\lambda R(\lambda R - 1)}}$ (d) $\sqrt{\frac{(\lambda R - 1)}{\lambda R}}$

[Hint : $\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = R\left[\frac{1}{1} - \frac{1}{n_2^2}\right]$

$$n_2 = \sqrt{\frac{\lambda R}{\lambda R - 1}} \text{]}$$

41. A dye absorbs a photon of wavelength λ and re-emits the same energy into two photons of wavelength λ_1 and λ_2 respectively. The wavelength λ is related to λ_1 and λ_2 as :

(a) $\lambda = \frac{\lambda_1\lambda_2}{(\lambda_1 + \lambda_2)^2}$ (b) $\lambda = \frac{\lambda_1 + \lambda_2}{\lambda_1\lambda_2}$

(c) $\lambda = \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}$ (d) $\frac{\lambda_1^2\lambda_2^2}{\lambda_1 + \lambda_2}$

42. The radii of maximum probability for $3s$, $3p$ and $3d$-electrons are in the order :

(a) $(r_{max})_{3s} > (r_{max})_{3p} > (r_{max})_{3d}$

(b) $(r_{max})_{3s} = (r_{max})_{3p} = (r_{max})_{3d}$

(c) $(r_{max})_{3d} > (r_{max})_{3p} > (r_{max})_{3s}$

(d) $(r_{max})_{3d} > (r_{max})_{3s} > (r_{max})_{3p}$

Following questions may have more than one correct options:

1. Select the correct relations on the basis of Bohr theory:

(a) velocity of electron $\propto \frac{1}{n}$ (b) frequency of revolution $\propto \frac{1}{n^3}$

(c) radius of orbit $\propto n^2 Z$ (d) force on electron $\propto \frac{1}{n^4}$

2. To which of the following species, the Bohr theory is not applicable?

(a) He (b) Li^{2+} (c) He^{2+} (d) H-atom

3. The magnitude of spin angular momentum of an electron is given by:

(a) $S = \sqrt{s(s+1)}\frac{h}{2\pi}$ (b) $S = s\frac{h}{2\pi}$

(c) $S = \frac{\sqrt{3}}{2} \times \frac{h}{2\pi}$ (d) $S = \pm\frac{1}{2} \times \frac{h}{2\pi}$

[Hint: Spin angular momentum $= \sqrt{s(s+1)}\frac{h}{2\pi}$

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)}\frac{h}{2\pi} = \frac{\sqrt{3}}{2} \times \frac{h}{2\pi} \text{]}$$

4. Select the correct configurations among the following:

(a) Cr $(Z = 24)$: [Ar] $3d^5, 4s^1$

(b) Cu $(Z = 29)$: [Ar] $3d^{10}, 4s^1$

(c) Pd $(Z = 46)$: [Kr] $4d^{10}, 5s^0$

(d) Pt $(Z = 78)$: [Xe] $4d^{10}\, 4s^2$

5. Which among the following statements is/are correct?
   (a) ψ^2 represents the atomic orbitals
   (b) The number of peaks in radial distribution is $(n-l)$
   (c) Radial probability density $\rho_{nl}(r) = 4\pi r^2 R_{nl}^2(r)$
   (d) A node is a point in space where the wave function (ψ) has zero amplitude
6. Select the correct statement(s) among the following:
   (i) Total number of orbitals in a shell with principal quantum number 'n' is n^2
   (ii) Total number of subshells in the n th energy level is n
   (iii) The maximum number of electrons in a subshell is given by the expression $(4l+2)$
   (iv) $m = l+2$, where l and m are azimuthal and magnetic quantum numbers
   (a) (i), (iii) and (iv) are correct
   (b) (i), (ii) and (iii) are correct
   (c) (ii), (iii) and (iv) are correct
   (d) (i), (ii) and (iv) are correct
7. Which among the following are correct about angular momentum of electron?
   (a) $2\hbar$ (b) $1.5\dfrac{h}{\pi}$ (c) $2.5\hbar$ (d) $0.5\dfrac{h}{\pi}$
8. Which of the following is/are incorrect for Humphrey lines of hydrogen spectrum?
   (a) $n_2 = 7 \rightarrow n_1 = 2$ (b) $n_2 = 10 \rightarrow n_1 = 6$
   (c) $n_2 = 5 \rightarrow n_1 = 1$ (d) $n_2 = 11 \rightarrow n_1 = 3$
9. In the Bohr's model of the atom:
   (a) the radius of n th orbit is proportional to n^2
   (b) the total energy of the electron in the n th orbit is inversely proportional to 'n'
   (c) the angular momentum of the electron is integral multiple of $h/2\pi$
   (d) the magnitude of potential energy of an electron in an orbit is greater than kinetic energy
10. Which among the following series is obtained in both absorption and emission spectrums?
   (a) Lyman series (b) Balmer series
   (c) Paschen series (d) Brackett series
11. The maximum kinetic energy of photoelectrons is directly proportional to . . . of the incident radiation. The missing word can be:
   (a) intensity (b) wavelength
   (c) wave number (d) frequency
12. Rutherford's experiment established that:
   (a) inside the atom there is a heavy positive centre
   (b) nucleus contains protons and neutrons
   (c) most of the space in an atom is empty
   (d) size of nucleus is very small
13. Which of the following orbital(s) lie in the xy-plane?
   (a) $d_{x^2-y^2}$ (b) d_{xy} (c) d_{xz} (d) d_{yz}
14. In which of the following sets of orbitals, electrons have equal orbital angular momentum?
   (a) $1s$ and $2s$ (b) $2s$ and $2p$ (c) $2p$ and $3p$ (d) $3p$ and $3d$
15. Which of the following orbitals have no spherical nodes?
   (a) $1s$ (b) $2s$ (c) $2p$ (d) $3p$
16. For a shell of principal quantum number $n = 4$, there are:
   (a) 16 orbitals (b) 4 subshells
   (c) 32 electrons (maximum) (d) 4 electrons with $l = 3$
17. The isotopes contain the same number of:
   (a) neutrons (b) protons
   (c) protons + neutrons (d) electrons
18. Which of the following species has less number of protons than the number of neutrons?
   (a) ${}^{12}_{6}C$ (b) ${}^{19}_{9}F$ (c) ${}^{23}_{11}Na$ (d) ${}^{24}_{12}Mg$
19. The angular part of the wave function depends on the quantum numbers are:
   (a) n (b) l (c) m (d) s
20. Which of the following species are expected to have spectrum similar to hydrogen?
   (a) He^+ (b) He^{2+} (c) Li^{2+} (d) Li^+
21. Which of the following statements is/are correct regarding a hydrogen atom?
   (a) Kinetic energy of the electron is maximum in the first orbit
   (b) Potential energy of the electron is maximum in the first orbit
   (c) Radius of the second orbit is four times the radius of the first orbit
   (d) Various energy levels are equally spaced

Answers

• Single correct option

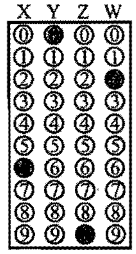
1. (c)	2. (d)	3. (c)	4. (b)	5. (a)	6. (d)	7. (d)	8. (d)
9. (b)	10. (c)	11. (b)	12. (c)	13. (a)	14. (a)	15. (b)	16. (c)
17. (d)	18. (b)	19. (b)	20. (a)	21. (c)	22. (b)	23. (a)	24. (b)
25. (a)	26. (b)	27. (b)	28. (a)	29. (b)	30. (c)	31. (b)	32. (b)
33. (b)	34. (c)	35. (c)	36. (d)	37. (c)	38. (b)	39. (c)	40. (b)
41. (c)	42. (a)						

• One or more than one correct options

1. (a, b, d)	2. (a, c)	3. (a, c)	4. (a, b, c)	5. (a, b, c, d)	6. (b)	7. (a, b, d)	8. (a, c, d)
9. (a, c, d)	10. (a)	11. (c, d)	12. (a, c, d)	13. (a, b)	14. (a, c)	15. (a, c)	16. (a, b, c)
17. (b, d)	18. (b, c)	19. (b, c)	20. (a, c)	21. (a, c)			

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the figure :



1. For Li^{2+}, when an electron falls from a higher orbit to nth orbit, all the three types of lines, *i.e.*, Lyman, Balmer and Paschen was found in the spectrum. Here, the value of 'n' will be:
2. The emission lines of hydrogen contains ten lines. The highest orbit in which the electron is expected to be found is :

   [**Hint :** Number of lines $= \frac{n(n-1)}{2} = 10$

   $\therefore \qquad n = 5$]
3. Total number of nodes present in $4d$ orbitals will be :
4. Spin multiplicity of nitrogen in ground state will be :
5. Orbital frequency of electron in nth orbit of hydrogen is twice that of 2nd orbit. The value of n is :
6. If kinetic energy of an electron is reduce by (1/9) then how many times its de Broglie wavelength will increase.
7. If electrons in hydrogen sample return from 7th shell to 4th shell then how many maximum number of lines can be observed in the spectrum of hydrogen.
8. An electron in Li^{2+} ion is in excited state (n_2). The wavelength corresponding to a transition to second orbit is 48.24 nm. From the same orbit, wavelength corresponding to a transition to third orbit is 142.46 nm. The value of n_2 is :
9. The energy corresponding to one of the lines in the Paschen series for H-atom is 18.16×10^{-20} J. Find the quantum numbers for the transition which produce this line.

   [**Hint :** $\Delta E = 2.18 \times 10^{-18}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

   $18.16 \times 10^{-20} = 2.18 \times 10^{-18}\left[\frac{1}{9} - \frac{1}{n^2}\right]$

   On solving, $n = 6$]
10. The angular momentum of electron in the shell in which the g-subshell first appears is $x \times \frac{h}{2\pi}$. The value of x will be :

    [**Hint :** $l = 4$ for g-subshell

    Thus, the subshell will first appear in $(n = l + 1 = 5)$ 5th shell.

    Angular momentum $(mvr) = n\frac{h}{2\pi}$

    $= 5\frac{h}{2\pi}$

    $\therefore \qquad n = 5$]

Answers

1. (1)	**2.** (5)	**3.** (3)	**4.** (4)	**5.** (1)	**6.** (3)	**7.** (6)	**8.** (5)
9. (6)	**10.** (5)						

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

The observed wavelengths in the line spectrum of hydrogen atom were first expressed in terms of a series by Johann Jakob Balmer, a Swiss teacher.

Balmer's empirical formula is:

$$\frac{1}{\lambda}=R_H\left[\frac{1}{2^2}-\frac{1}{n^2}\right] n=3,4,5,\ldots$$

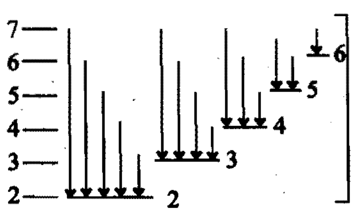
$R_H = 109678\ \text{cm}^{-1}$ *is the Rydberg constant.*

Niels Bohr derived this expression theoretically in 1913. *The formula is generalised to any one electron atom/ion.*

Answer the following questions:

1. Calculate the longest wavelength in Å (1 Å = 10^{-10} m) in the Balmer series of singly ionized helium He^+. Select the correct answer. Ignore the nuclear motion in your calculation.
   (a) 2651 Å (b) 1641.1 Å
   (c) 6569 Å (d) 3249 Å
   [**Hint:** $\frac{1}{\lambda_{He^+}}=R_H Z^2\left[\frac{1}{2^2}-\frac{1}{3^2}\right]$
   $=109678\times 4\left[\frac{5}{36}\right]$
   $\lambda_{He^+}=1641.1\ \text{Å}$]

2. How many lines in the spectrum will be observed when electrons return from 7th shell to 2nd shell?
   (a) 13 (b) 14 (c) 15 (d) 16
   [**Hint:** Number of lines in the spectrum
   $=\frac{(n_2-n_1)(n_2-n_1+1)}{2}$
   $=\frac{(7-2)(7-2+1)}{2}=15$



15 lines in the spectrum.]

3. The wavelength of first line of Balmer spectrum of hydrogen will be:
   (a) 4340 Å (b) 4101 Å (c) 6569 Å (d) 4861 Å
   [**Hint:** $\frac{1}{\lambda}=R_H\left[\frac{1}{2^2}-\frac{1}{n^2}\right]$
   for first line $n = 3$,
   $\therefore \quad \frac{1}{\lambda}=109678\left[\frac{1}{2^2}-\frac{1}{3^2}\right]$
   $\lambda = 6569\ \text{Å}$]

4. In which region of electromagnetic spectrum does the Balmer series lie?
   (a) UV (b) Visible
   (c) Infrared (d) Far infrared

5. Which of the following is not correctly matched?
   (a) H_α — 6569 Å (Red) (b) H_β — 4861 Å (Blue)
   (c) H_γ — 4340 Å (Orange) (d) H_δ — 4101 Å (Violet)

• Passage 2

A formula analogous to the Rydberg formula applies to the series of spectral lines which arise from transitions from higher energy level to the lower energy level of hydrogen atom.

A muonic hydrogen atom is like a hydrogen atom in which the electron is replaced by a heavier particle, the 'muon'. The mass of the muon is about 207 *times the mass of an electron, while the charge remains same as that of the electron. Rydberg formula for hydrogen atom is:*

$$\frac{1}{\lambda}=R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right](R_H=109678\ \text{cm}^{-1})$$

Answer the following questions:

1. Radius of first Bohr orbit of muonic hydrogen atom is:
   (a) $\frac{0.259}{207}$ Å (b) $\frac{0.529}{207}$ Å
   (c) 0.529×207 Å (d) 0.259×207 Å

2. Energy of first Bohr orbit of muonic hydrogen atom is:
   (a) $-\frac{13.6}{207}$ eV (b) -13.6×207 eV
   (c) $+\frac{13.6}{207}$ eV (d) $+13.6\times 207$ eV

3. Ionization energy of muonic hydrogen atom is:
   (a) $+\frac{13.6}{207}$ eV (b) $+13.6\times 207$ eV
   (c) $-\frac{13.6}{207}$ eV (d) -13.6×207 eV

4. Angular momentum of 'muon' in muonic hydrogen atom may be given as:
   (a) $\frac{h}{\pi}$ (b) $\frac{h}{2\pi}$ (c) $\frac{h}{4\pi}$ (d) $\frac{h}{6\pi}$

5. Distance between first and third Bohr orbits of muonic hydrogen atom will be:
   (a) $\frac{0.529}{207}\times 2$ Å (b) $\frac{0.529}{207}\times 7$ Å
   (c) $\frac{0.529}{207}\times 8$ Å (d) $\frac{0.529}{207}$ Å

• Passage 3

Nuclei that have 2, 8, 20, 28, 50, 82 *and* 126 *neutrons or protons are more abundant and more stable than other nuclei of similar mass. It is suggested that in the nuclear structure of the numbers* 2, 8, 20, 28, 50, 82 *and* 126, *which have become known as magic numbers, the nuclei possessing magic numbers are spherical and have zero quadruple moment and hence they are highly stable. Nuclear shells are filled when there are* 2, 8, 20, 28, 50, 82 *and* 126 *neutrons or protons in a nucleus. In even-even nuclei all the neutrons and protons are paired and cancel out spin and orbital angular momenta.*

Answer the following questions regarding the stability of nucleus:

1. Which of the following element(s) is/are stable though having odd number of neutrons and protons?
   (a) ${}^{6}_{3}Li$ (b) ${}^{11}_{5}B$ (c) ${}^{4}_{2}He$ (d) ${}^{14}_{7}N$
2. Stable nuclei having number of neutrons less than number of protons are:
   (a) ${}^{1}_{1}H$ (b) ${}^{3}_{2}He$ (c) ${}^{11}_{5}B$ (d) ${}^{11}_{6}C$
3. Doubly magic nucleus is . . . .
   (a) ${}^{207}_{82}Pb$ (b) ${}^{206}_{82}Pb$ (c) ${}^{208}_{82}Pb$ (d) ${}^{209}_{83}Bi$
4. Which among the following has unstable nucleus?
   (a) ${}^{14}_{7}N$ (b) ${}^{15}_{7}N$ (c) ${}^{13}_{7}N$ (d) ${}^{16}_{8}O$
5. Which of the following has zero spin and angular momentum?
   (a) ${}^{40}_{20}Ca$ (b) ${}^{3}_{1}H$ (c) ${}^{14}_{6}C$ (d) ${}^{37}_{17}Cl$

• Passage 4

The substances which contain species with unpaired electrons in their orbitals behave as paramagnetic substances. Such substances are weakly attracted by the magnetic field. The paramagnetism is expressed in terms of magnetic moment. The magnetic moment is related to the number of unpaired electrons according to the following relation:

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}\ BM$$

where, n = number of unpaired electrons.

BM stands for Bohr magneton, a unit of magnetic moment.

$$1\,BM = \frac{eh}{4\pi mc} = 9.27 \times 10^{-24}\ Am^2 \text{ or } J\,T^{-1}$$

Answer the following questions:

1. Which of the following ions has the highest magnetic moment?
   (a) Fe^{2+} (b) Mn^{2+} (c) Cr^{3+} (d) V^{3+}
2. Which of the following ions has magnetic moment equal to that of Ti^{3+}:
   (a) Cu^{2+} (b) Ni^{2+} (c) Co^{2+} (d) Fe^{2+}
3. An ion of a *d*-block element has magnetic moment 5.92 BM Select the ion among the following:
   (a) Zn^{2+} (b) Sc^{3+} (c) Mn^{2+} (d) Cr^{3+}
4. In which of these options do both constituents of the pair have the same magnetic moment?
   (a) Zn^{2+} and Cu^{+} (b) Co^{2+} and Ni^{2+}
   (c) Mn^{4+} and Co^{2+} (d) Mg^{2+} and Sc^{+}
5. Which of the following ions are diamagnetic?
   (a) He^{2+} (b) Sc^{3+} (c) Mg^{2+} (d) O^{2-}

• Passage 5

At the suggestion of Ernest Rutherford, Hans Geiger and Ernest Marsden bombarded a thin gold foil by α-particles from a polonium source. It was expected that α-particles would go right through the foil with hardly any deflection. Although, most of the alpha particles indeed were not deviated by much, a few were scattered through very large angles. Some were even scattered in the backward direction. The only way to explain the results, Rutherford found, was to picture an atom as being composed of a tiny nucleus in which its positive charge and nearly all its mass are concentrated. Scattering of α-particles is proportional to target thickness and is inversely proportional to the fourth power of sin $\frac{\theta}{2}$, where, θ is scattering angle. Distance of closest approach may be calculated as:

$$r_{min} = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 K}$$

where, K = kinetic energy of α-particles.

Answer the following questions:

1. Rutherford's α-particle scattering experiment led to the conclusion that:
   (a) mass and energy are related
   (b) mass and positive charge of an atom are concentrated in the nucleus
   (c) neutrons are present in the nucleus
   (d) atoms are electrically neutral
2. From the α-particle scattering experiment, Rutherford concluded that:
   (a) α-particles can approach within a distance of the order of 10^{-14} m of the nucleus
   (b) the radius of the nucleus is less than 10^{-14} m
   (c) scattering follows Coulomb's law
   (d) the positively charged parts of the atom move with extremely high velocities
3. Rutherford's scattering formula fails for very small scattering angles because:
   (a) the gold foil is very thin
   (b) the kinetic energy of α-particles is very high
   (c) the full nuclear charge of the target atom is partially screened by its electron
   (d) there is strong repulsive force between the α-particles and nucleus of the target
4. Alpha particles that come closer to the nuclei:
   (a) are deflected more (b) are deflected less
   (c) make more collision (d) are slowed down more
5. Which of the following quantities will be zero for alpha particles at the point of closest approach to the gold atom, in Rutherford's scattering of alpha particles?
   (a) Acceleration (b) Kinetic energy
   (c) Potential energy (d) Electrical energy

• Passage 6

The splitting of spectral lines by a magnetic field is called the Zeeman effect after the Dutch physicist Pieter Zeeman. The Zeeman effect is a vivid confirmation of space quantization. Magnetic quantum number 'm' was introduced during the study of Zeeman effect. 'm' can have the $(2l+1)$ values $(-l, 0, +l)$. Magnetic quantum number represents the orientation of atomic orbitals in three-dimensional space. The normal Zeeman effect consists of the splitting of a spectral line of frequency ν_0 into three components, i.e.,

$$\nu_1 = \nu_0 - \frac{e}{4\pi m}B;\ \nu_2 = \nu_0;\ \nu_3 = \nu_0 + \frac{e}{4\pi m}B$$

Here, B is magnetic field.

Answer the following questions:

1. Which of the following statements is incorrect with reference to the Zeeman effect?
   (a) In a magnetic field, the energy of a particular atomic state depends on the values of 'm' and 'n'
   (b) Zeeman effect is used to calculate the e/m ratio for an electron
   (c) Individual spectral lines split into separate lines. The distance between them is independent of the magnitude of the magnetic field
   (d) The Zeeman effect involves splitting of a spectral line of frequency ν_0 into three components
2. A d-subshell in an atom in the presence and absence of magnetic field is:
   (a) five-fold degenerate, non-degenerate
   (b) seven-fold degenerate, non-degenerate
   (c) five-fold degenerate, five-fold degenerate
   (d) non-degenerate, five-fold degenerate
3. Which among the following is/are correct about the orientation of atomic orbitals in space?
   (a) s-orbitals has single orientation
   (b) d-subshell orbitals have three orientations along x, y and z directions
   (c) f-subshell have seven orientations in their orbitals
   (d) None of the above
4. Zeeman effect explains splitting of spectral lines in:
   (a) magnetic field (b) electric field
   (c) both (a) and (b) (d) none of these
5. In presence of magnetic field, d-suborbit is:
   (a) five-fold degenerate (b) three-fold degenerate
   (c) seven-fold degenerate (d) non-degenerate

Passage 7

Spin angular momentum of an electron has no analogue in classical mechanics. However, it turns out that the treatment of spin angular momentum is closely analogous to the treatment of orbital angular momentum.

$$\text{Spin angular momentum} = \sqrt{s(s+1)}\,\hbar$$

$$\text{Orbital angular momentum} = \sqrt{l(l+1)}\,\hbar$$

Total spin of an atom or ion is a multiple of $\frac{1}{2}$. Spin multiplicity is a factor to confirm the electronic configuration of an atom or ion.

$$\text{Spin multiplicity} = (2\Sigma s + 1)$$

Answer the following questions:

1. Total spin of Mn^{2+} $(Z = 25)$ ion will be:
   (a) $\frac{3}{2}$ (b) $\frac{1}{2}$ (c) $\frac{5}{2}$ (d) $\frac{7}{2}$
2. Which of the following electronic configurations have four spin multiplicity?
   (a) | ↑ | ↑ | ↑ | (b) | ↑ | ↑ | ↓ |
   (c) | ↑ | ↓ | ↑ | (d) | ↓ | ↓ | ↓ |
3. Which of the following quantum numbers is not derived from Schrödinger wave equation?
   (a) Principal (b) Azimuthal
   (c) Magnetic (d) Spin
4. In any subshell, the maximum number of electrons having same value of spin quantum number is:
   (a) $\sqrt{l(l+1)}$ (b) $l+2$ (c) $2l+1$ (d) $4l+2$
5. The orbital angular momentum for a $2p$-electron is:
   (a) $\sqrt{3}\,\hbar$ (b) $\sqrt{6}\,\hbar$ (c) zero (d) $\sqrt{2}\,\frac{h}{2\pi}$

• Passage 8

Dual nature of matter was proposed by de Broglie in 1923, it was experimentally verified by Davisson and Germer by diffraction experiment. Wave character of matter has significance only for microscopic particles. de Broglie wavelength or wavelength of matter wave can be calculated using the following relation:

$$\lambda = \frac{h}{mv}$$

where, 'm' and 'v' are the mass and velocity of the particle.

de Broglie hypothesis suggested that electron waves were being diffracted by the target, much as X-rays are diffracted by planes of atoms in the crystals.

Answer the following questions:

1. Planck's constant has same dimension as that of:
   (a) work (b) energy
   (c) power (d) angular momentum
2. Wave nature of electrons is shown by:
   (a) photoelectric effect (b) Compton effect
   (c) diffraction experiment (d) Stark effect
3. de Broglie equation is obtained by combination of which of the following theories?
   (a) Planck's quantum theory
   (b) Einstein's theory of mass-energy equivalence
   (c) Theory of interference
   (d) Theory of diffraction
4. Which among the following is not used to calculate the de Broglie wavelength?
   (a) $\lambda = \frac{c}{\nu}$ (b) $\lambda = \frac{h}{mv}$
   (c) $\lambda = \frac{h}{\sqrt{2Em}}$ (d) $\lambda = \frac{h}{\sqrt{2qVm}}$
5. The wavelength of matter waves associated with a body of mass 1000 g moving with a velocity of 100 m/sec is:
   (a) 6.62×10^{-39} cm (b) 6.62×10^{-36} cm
   (c) 6.626×10^{-36} m (d) 3.31×10^{-32} m
6. An electron microscope is used to probe the atomic arrangements to a resolution of 5 Å. What should be the electric potential to which the electrons need to be accelerated ? **(VITEEE 2008)**
   (a) 2.5 V (b) 6 V
   (c) 2.5 kV (d) 5 kV

• Passage 9

Orbital is the region in an atom where the probability of finding the electron is maximum. It represents three-dimensional motion of an electron around the nucleus. Orbitals do not specify a definite path according to the uncertainty principle. An orbital is described with the help of wave function ψ. Whenever an electron is described by a wave function, we say that an electron occupies that orbital. Since, many wave functions are possible for an electron, there are many atomic orbitals in an atom. Orbitals have different shapes; except s-orbitals, all other orbitals have directional character. Number of spherical nodes in an orbital is equal to $(n-l-1)$. Orbital angular momentum of an electron is $\sqrt{l(l+1)}\,\hbar$.

Answer the following questions:

1. Which of the following orbitals is not cylindrically symmetrical about z-axis?
   (a) $3d_{z^2}$ (b) $4p_z$ (c) $6s$ (d) $3d_{yz}$
2. The nodes present in $5p$-orbital are:
   (a) one planar, five spherical (b) one planar, four spherical
   (c) one planar, three spherical (d) four spherical
3. When an atom is placed in a magnetic field, the possible number of orientations for an orbital of azimuthal quantum number 3 is:
   (a) three (b) one (c) five (d) seven
4. Orbital angular momentum of f-electrons is:
   (a) $\sqrt{2}\,\hbar$ (b) $\sqrt{3}\,\hbar$ (c) $\sqrt{12}\,\hbar$ (d) $2\,\hbar$
5. Which of the following orbitals has/have two nodal planes?
   (a) d_{xy} (b) d_{yz} (c) $d_{x^2-y^2}$ (d) All of these

• Passage 10

The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2. The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

(IIT 2010)

Answer the following questions:

1. The state S_1 is:
   (a) $1s$ (b) $2s$ (c) $2p$ (d) $3s$
   [**Hint:** $2s$ is symmetrical having one radial node.]
2. Energy of the state S_1 in units of the hydrogen atom ground state energy is:
   (a) 0.75 (b) 1.50 (c) 2.25 (d) 4.50
   [**Hint:** $\dfrac{E_{Li^{2+}}(2s)}{E_H} = \dfrac{-\frac{9}{4}\times 13.6}{-13.6} = 2.25$]
3. The orbital angular momentum quantum number of the state S_2 is:
   (a) 0 (b) 1 (c) 2 (d) 3
   [**Hint:** Orbital angular momentum quantum number of $3p$ subshell, *i.e.*, $l = 1$
   $$\underset{2s}{S_1} \xrightarrow{\text{Transition}} \underset{3p}{S_2}$$]

Answers

Passage 1.	1. (b)	2. (c)	3. (c)	4. (b)	5. (c)	
Passage 2.	1. (b)	2. (b)	3. (b)	4. (b)	5. (c)	
Passage 3.	1. (a, d)	2. (a, b)	3. (c)	4. (c)	5. (a)	
Passage 4.	1. (b)	2. (a)	3. (c)	4. (a, c)	5. (b, c, d)	
Passage 5.	1. (b)	2. (a, b, c)	3. (c, d)	4. (a)	5. (b)	
Passage 6.	1. (b)	2. (d)	3. (a, c)	4. (a)	5. (d)	
Passage 7.	1. (c)	2. (a)	3. (d)	4. (c)	5. (d)	
Passage 8.	1. (d)	2. (c)	3. (a, b)	4. (a)	5. (c)	6. (b)
Passage 9.	1. (d)	2. (c)	3. (d)	4. (c)	5. (d)	
Passage 10.	1. (b)	2. (c)	3. (b)			

SELF ASSESSMENT

ASSIGNMENT NO. 2

SECTION-I

Straight Objective Type Questions

This section contains 11 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Which one of the following leads to third line of Balmer spectrum from red end (For hydrogen atom)?
(a) $2 \longrightarrow 5$ (b) $5 \longrightarrow 2$ (c) $3 \longrightarrow 2$ (d) $4 \longrightarrow 1$

2. The orbital angular momentum and angular momentum (classical analogue) for the electron of 4s-orbital are respectively, equal to:
(a) $\sqrt{12}\frac{h}{2\pi}$ and $\frac{h}{2\pi}$ (b) zero and $\frac{2h}{\pi}$
(c) $\sqrt{6}h$ and $\frac{2h}{\pi}$ (d) $\sqrt{2}\frac{h}{2\pi}$ and $\frac{3h}{2\pi}$

3. A sample of hydrogen atom is excited to $n = 4$ state. In the spectrum of emitted radiation, the number of lines in the ultraviolet and visible regions are respectively:
(a) 3 : 2 (b) 2 : 3 (c) 1 : 3 (d) 3 : 1

4. Number of de Broglie waves made by a Bohr electron in an orbit of maximum magnetic quantum number + 2 is:
(a) 1 (b) 2 (c) 3 (d) 4

5. First line of Lyman series of hydrogen atom occurs at $\lambda = x$ Å. The corresponding line of He^+ will occur at:
(a) $4x$ (b) $3x$ (c) $x/3$ (d) $x/4$

6. Electronic transition in He^+ ion takes from n_2 to n_1 shell such that;
$$2n_2 + 3n_1 = 18 \quad ...(i)$$
$$2n_2 - 3n_1 = 6 \quad ...(ii)$$
then what will be the total number of photons emitted when electrons transit to n_1 shell?
(a) 21 (b) 15 (c) 20 (d) 10

7. Which of the following sets of quantum numbers is not possible for an electron ? **[PET (Raj.) 2008]**
(a) $n = 1, l = 0, m_l = 0, m_s = -1/2$
(b) $n = 2, l = 1, m_l = 0, m_s = -1/2$
(c) $n = 1, l = 1, m_l = 0, m_s = +1/2$
(d) $n = 2, l = 1, m_l = 0, m_s = +1/2$

8. The average life of an excited state of hydrogen atom is of the order of 10^{-8} sec. The number of revolutions made by an electron when it returns from $n = 2$ to $n = 1$ is:
(a) 2.28×10^6 (b) 22.8×10^6 (c) 8.23×10^6 (d) 2.82×10^6

9. The wave number of a particular spectral line in the atomic spectrum of a hydrogen like species increases 9/4 times when deuterium nucleus is introduced into its nucleus, then which of the following will be the initial hydrogen like species?
(a) Li^{2+} (b) Li^+ (c) He^+ (d) Be^{3+}

10. Energy of electron in the first Bohr orbit of H-atom is -313.6 kcal mol^{-1}; then the energy in second Bohr orbit will be:
(a) $+313.6$ kcal mol^{-1} (b) -78.4 kcal mol^{-1}
(c) -34.84 kcal mol^{-1} (d) -12.5 kcal mol^{-1}

11. Which phenomenon best supports the theory that matter has a wave nature ? **(VITEEE 2008)**
(a) Electron momentum (b) Electron diffraction
(c) Photon momentum (d) Photon diffraction

SECTION-II

Multiple Answers Type Objective Questions

12. Which of the following is/are correct?
(a) An electron in excited state cannot absorb a photon
(b) Energy of electrons depends only on the principal quantum numbers
(c) Energy of electrons depends only on the principal quantum number for hydrogen atom
(d) Difference in potential energy of two shells is equal to the difference in kinetic energy of these shells

13. Which of the following statements is/are correct?
(a) Energy of $4s$, $4p$, $4d$ and $4f$ are same for hydrogen
(b) Angular momentum of electron = $I\omega$
(c) For all values of 'n', the p-orbitals have the same shape
(d) Orbital angular momentum = $nh/2\pi$

14. Which of the following orbitals are associated with angular nodes?
(a) f (b) d (c) p (d) s

15. The correct statement(s) among the following is/are:
(a) All d-orbitals except d_{z^2} have two angular nodes
(b) $d_{x^2-y^2}$, d_{z^2} lie on the axes
(c) The degeneracy of p-orbitals remains unaffected in the presence of external magnetic field
(d) d-orbitals have 3-fold degeneracy

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.
(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** Kinetic energy of photoelectrons increases with increase in the frequency of incident radiation.
Because
Statement-2: The number of photoelectrons ejected increases with increase in intensity of incident radiation.

17. **Statement-1:** Photoelectric effect is easily pronounced by caesium metal.
Because
Statement-2: Photoelectric effect is easily pronounced by the metals having high ionization energy.

18. **Statement-1:** Electrons in K-shell revolve in circular orbit.
Because
Statement-2: Principal quantum number 'n' is equal to 1 for the electrons in K-shell.

19. **Statement-1:** Orbit and orbital are synonymous.
Because
Statement-2: Orbit is the path around the nucleus in which electron revolves.

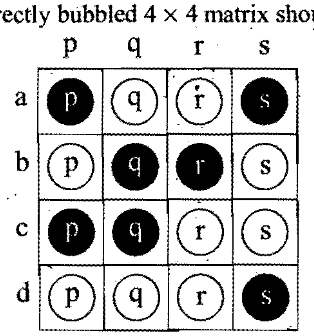
20. **Statement-1:** $C_6 = 1s^2, 2s^1, 2p^3$ is the electronic configuration in first excited state.
Because
Statement-2: Maximum energy by an electron is possessed in its ground state.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statements given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then the correctly bubbled 4 × 4 matrix should be as follows:



21. Match the Column-I with Column-II:

	Column-I	Column-II
(a)	$4s$	(p) Circular orbit around nucleus
(b)	$4p$	(q) Non-direction orbitals
(c)	$1s$	(r) Angular momentum = $\frac{2h}{\pi}$
(d)	$3d$	(s) Number of radial node = 0

22. Match the properties of Column-I with the formulae in Column-II:

Column-I	Column-II
(a) Angular momentum of electron	(p) $\sqrt{l(l+1)}\frac{h}{2\pi}$
(b) Orbital angular momentum	(q) $I\omega$
(c) Wavelength of matter wave	(r) $\frac{nh}{2\pi}$
(d) Quantised value(s)	(s) h/p

23. Match the Column-I with Column-II:

	Column-I		Column-II
(a)	Electrons cannot exist in the nucleus	(p)	de Broglie wave
(b)	Microscopic particles in motion are associated with	(q)	Electromagnetic wave
(c)	No medium is required for propagation	(r)	Uncertainty principle
(d)	Concept of orbit was replaced by orbital	(s)	Transverse wave

SECTION-V

Linked Comprehension Type Questions

A chemist was performing an experiment to study the effect of varying voltage on the velocity and de Broglie wavelength of the electrons. In first experiment, the electron was accelerated through a potential difference of 1 kV and in second experiment, it was accelerated through a potential difference of 2 kV.

The wavelength of de Broglie waves associated with electron is given by:

$$\lambda = \frac{h}{\sqrt{2qVm}}$$

where, V is the voltage through which an electron is accelerated.

Putting the values of h, m and q we get:

$$\lambda = \frac{12.3}{\sqrt{V}}\text{Å}$$

Answer the following questions:

24. The wavelength of electron will be:
(a) 1.4 times in first case than in second case
(b) 1.4 times in second case than in first case
(c) double in second case than in first case
(d) double in first case than in second case

25. In order to get half velocity of electrons in second case, the applied potential will be:
(a) 0.25 kV (b) 2 kV (c) 0.5 kV (d) 0.75 kV

26. The velocity of electron will be:
(a) same in both cases
(b) 1.4 times in second experiment than in first experiment
(c) double in second experiment than in first experiment
(d) four times in the second case than in first case

Answers

1. (b)	2. (b)	3. (a)	4. (c)	5. (d)	6. (d)	7. (c)	8. (c)
9. (d)	10. (b)	11. (b)	12. (a, c, d)	13. (a, b, c)	14. (a, b, c)	15. (a, b, c)	16. (b)
17. (c)	18. (b)	19. (d)	20. (c)	21. (a-p, q,r) (b-r) (c-p,q) (d-s)			
22. (a-q,r) (b-p) (c-s) (d-q,r)		23. (a-r) (b-p) (c-q,s) (d-r)		24. (a)	25. (a)	26. (b)	